ASSESSMENT REPORT ON

ETHYLENE

FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

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ASSESSMENT REPORT ON ETHYLENE FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

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SUMMARY

Ethylene is a naturally occurring compound in ambient air. It is produced at low levels by soil microorganisms, algae, lichens and plants. Other natural sources of ethylene are volcanic activity and combustion in forest and grass fires. In Alberta, the concentration in ambient air resulting from these natural sources is typically low, approximating 12 $\mu g\ m^{-3}$ (equal to 10 parts per billion).

Anthropogenic sources of ethylene such as combustion of fossil fuels, and processing of natural gas in petrochemical facilities (e.g. production of plastics) result in emissions that may substantially increase ambient air ethylene concentrations. Alberta industrial facilities reported ethylene releases of 1,238 tonnes in 1999. Monitoring of ambient ethylene around petrochemical facilities is a method that gives an indication of releases of ethylene into the environment.

There are many methods of collecting and measuring ambient ethylene. The most important aspect of this process is a good quality assurance and quality control program. The samples must be collected using methods that prevent contamination or loss then must be analysed using methods that will ensure consistency of results. The Laboratory Data Quality Assurance Policy in effect in Alberta was implemented to ensure analytical data and data from different sources are reliable, of consistent quality and that data is consistent with national and international standards.

Levels of ethylene as low as 12 $\mu g\ m^{-3}$ are known to affect vegetation; as a result, increases in ambient ethylene levels have the potential to affect Alberta vegetation. Ethylene affects vegetation at levels several orders of magnitude lower than levels that affect humans and animals. Therefore, guidelines protective of vegetation would also be protective in terms of human health.

This document updates the scientific review completed in 1997. It includes information on industrial releases of ethylene in Alberta, measurement and monitoring of ethylene including ambient levels of ethylene in the environment. In addition, there is an extensive section on research on the effects of ethylene on vegetation.

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1.0 INTRODUCTION

Ethylene is emitted into the atmosphere from a number of natural and anthropogenic sources. It is a potent regulator of plant growth and development and may have substantial effects at low concentrations in ambient air. As ethylene affects vegetation at levels several orders of magnitude lower than levels that affect humans and animals, the focus of the review was on vegetation effects (NRC, 1985; US EPA, 1992; Health Canada, 2001).

The initial review of the literature indicated that there was insufficient data of direct relevance to Alberta for the development of a full guideline for ethylene. Therefore, a research project examining the dose-response relationships between ethylene exposure and growth effects on various Alberta crops (Alberta Ethylene Crop Research Project) was conducted at the Alberta Research Council in Vegreville to provide data relevant to Alberta. The provincial government and the petrochemical industries in Alberta jointly sponsored this project.

This document updates the June 1997 review and analysis, incorporates results of the research project and presents a summary of the scientific literature regarding sources, ambient ethylene levels in rural, industrial and urban settings, and potential environmental effects of ethylene. The information in this document is for use in finalizing Alberta's ambient air objective for ethylene.

2.0 PHYSICAL AND CHEMICAL CHARACTERISTICS OF ETHYLENE

2.1 Physical and Chemical Characteristics, Registry Numbers

Synonyms for ethylene include ethene, bicarburretted hydrogen, elayl, acetene, and olefiant gas. The physical and chemical characteristics, and the various registry numbers, for ethylene are presented in Table 2.1.

Table 2.1 Registry numbers and physical and chemical characteristics of Ethylene†

Molecular Formula	C_2H_4
CAS Number	74-85-1
STCC Number	4905734
Melting Point (°C)	-169.2
Specific Gravity (at -104.0°C)	0.566
Vapour Density (at 25°C)	0.978
Molecular Weight (g $mole^{-1}$)	28.05
OHM-TADS Number	7216713
UN Numbers - Ethylene Gas	1962
- Ethylene Liquid	1038
Boiling Point (°C)	-103.7
Solubility in Water (mg l^{-1}, at 0°C)	131
Odour Threshold (mg m^{-1})	10^2 to 10^3
Log $_{10}$ Octanol Water Partition Coefficient††	1.13
Colorless gas, with a sweet odour and taste	

† Verschueren (1983)

†† Stahl (1969; cited in National Research Council, 1985)

2.2 Conversion Factors Used in this Review

There is a wide diversity of units of concentration used in the scientific literature. The concentration of ethylene in air may be expressed on a volume to volume (v/v), weight to volume (w/v), or weight to weight (w/w) basis. The familiar units of parts per million (ppm) and parts per billion (ppb) are measures in v/v; that is 1 ppm of ethylene is the concentration resulting from the presence of 1 µl of ethylene in a total volume of 1 litre (1,000,000 µl). Parts per billion is a concentration 1000-fold lower than ppm, and parts per trillion is a 1000-fold lower concentration than ppb.

Occasionally, concentrations of organic gases are expressed on the basis of the concentration of carbon in air. Examples include ppbC (parts per billion carbon) and pptC. Since ethylene

contains 2 carbon atoms, the concentration of 1 ppm ethylene is equivalent to 2 ppm carbon (2 ppmC), assuming the absence of other carbon-containing gases.

In Alberta guidelines, air contaminant concentrations are expressed in the units of $\mu g\ m^{-3}$. This is an expression in terms of weight to volume (w/v). In this document, all concentrations presented in original references have been converted using the following conversion factors at 1.0 atmospheric pressure and a temperature of 25°C[†]:

1 ppm = 1,150 $\mu g\ m^{-3}$	1 ppbC = 0.575 $\mu g\ m^{-3}$
1 ppb = 1.15 $\mu g\ m^{-3}$	1 pptv = 0.00115 $\mu g\ m^{-3}$
1 $\mu l\ l^{-1}$ = 1,150 $\mu g\ m^{-3}$	[††]1 Pa = 11,350 $\mu g\ m^{-3}$

In the sections of this document which discuss concentrations of ethylene in water, concentrations are expressed in micrograms per litre of water ($\mu g\ l^{-1}$), or in the cases of very low concentrations, as nanograms per litre ($ng\ l^{-1}$).

[†]One atmosphere at 25°C contains 4.09×10^{-2} moles L^{-1}. In units of mass, 1 ppm = (40.9) x (molecular weight) $\mu g\ m^{-3}$.

[††]Pa is *the pascal*, the SI unit for pressure.

3.0 IDENTIFICATION AND CHARACTERIZATION OF ETHYLENE SOURCES

Microbes and plants naturally produce ethylene. Ethylene is also produced from combustion of organic compounds, both in natural processes (e.g. forest fires) and as a result of human activity (fossil fuel combustion, processing of natural gas). In plants, ethylene functions as a plant hormone, and affects growth and development at concentrations 100 to 1,000,000 times lower than other hydrocarbons (Abeles, 1973). Plants respond to environmental variations and stresses by modulating both the production of and response to ethylene.

On a global scale, it has been estimated that 18 to 45 x 10^6 tonnes are released annually into the atmosphere (Sawada and Totsuka, 1986), of which 74% is attributed to natural sources and 26% to anthropogenic sources. Of the anthropogenic portion, 77% is attributed to biomass burning, while 21% is attributed to the burning of fossil fuels (Sawada and Totsuka, 1986).

3.1 Natural Production of Ethylene

3.1.1 Soil Microorganisms

Ethylene is produced in the soil as a by-product of microbial (bacterial and fungal) degradation of organic matter, and by synthesis within the microbes as a result of normal metabolic activity. The metabolic pathways of microbial ethylene production have been described by Bird and Lynch (1974), and Primrose (1979).

Only a subset of the total complement of soil bacteria and fungi are capable of producing ethylene (DaSilva *et al.*, 1974; Cook and Smith, 1977; Sutherland and Cook, 1980). Ethylene producing microbes live in a wide variety of ecosystems (e.g. within southeastern coastal plain and coniferous forest soils). The O-horizon (the upper soil layer, high in organic matter content) of forest soils in Finland was found to release up to 0.001 $\mu g\ cm^{-3}$ (soil) hr^{-1} (Weber *et al.*, 1983). Ethylene production in soil varies in response to a wide number of environmental variables, including temperature, soil moisture content, organic matter content, soil amendments (e.g. manure), compaction, and oxygen content (Burford, 1975; Cook and Smith, 1977; Campbell and Moreau, 1979; Lindberg *et al.*, 1979; Lynch and Harper, 1980). Anaerobic conditions (<2% oxygen) in the soil resulted in an increase in the amount of ethylene present in the soil, this ethylene was the result of microbial action (Smith and Restall, 1971, Sexstone and Mains, 1990). As a result of this environmental variability, microbial synthesis of ethylene varies naturally within the ecosystem. Physiologically active levels of ethylene may accumulate naturally in coniferous forest soils, where both tree root and microbial (fungal) growth are affected (Lindberg *et al.*, 1979).

3.1.2 Higher Plants

The biosynthetic pathway of ethylene production in plants is well understood, and is presented in detail by Abeles *et al.* (1992) and Imaseki (1991). As a hormone, synthesis (and hence release) of ethylene is often initiated to stimulate naturally occurring processes. Fruit ripening (climacteric ethylene synthesis and release) is the classic example of this process (Abeles *et al.*, 1992; Rogiers *et al.*, 1998; Rogiers and Knowles, 1999; Flores *et al.*, 2001). Alternatively, the presence of or production of other plant hormones such as auxin can induce ethylene production (Grossmann and Hansen, 2001).

Ethylene production is regulated at a number of metabolic steps, such that increases or decreases in production can be controlled in response to environmental signals. Stress, such as flooding, wind or other mechanical bending (e.g. lodging), wounding (mechanical and pathogenic attack), and chemical exposure (e.g. ozone), tends to increase ethylene production (Abeles, 1982; Hyodo, 1991; Mattoo and White, 1991; O'Donnell *et al.*, 1996; Kauppi *et al.*, 1998; Beltrano *et al.*, 1999; Barker, 1999; Kume *et al.*, 2000). Elevated CO_2 levels also promote ethylene biosynthesis in plants (Finlayson and Reid, 1994). As global CO_2 levels rise, ambient, background ethylene levels may also rise, which may in turn affect vegetation on local, regional and global scales.

Wheeler *et al.* (1996) investigated plant emission of ethylene in a hyperbaric chamber and estimated that ethylene emissions during vegetative growth were; 7-8 nl g^{-1} dry weight per hour with wheat and 15 nl g^{-1} dry weight per hour with lettuce.

Diurnal variations in endogenous ethylene levels occur in some plant species. Often ethylene emissions increase with the change from dark condition to light condition and/or vice versa (El-Beltagy and Hall, 1974; Kapuya and Hall, 1977; Voesenek *et al.*, 1990), while in others, ethylene emissions are constant throughout the day (Foster *et al.*, 1992). Rates of synthesis vary by species, tissue type (e.g. leaf, flower) and age of the plant. Emissions from several hard and soft wood species in dry and swamp areas of Louisiana ranged from below the detection limits (ca. 10 mg kg^{-1} hr^{-1}) to 30 mg kg^{-1} hr^{-1}, which resulted in ambient air background levels of 0.4 to 0.5 µg m^{-3} (Khalil and Rasmussen, 1992).

3.1.3 Algae and Lichens

The unicellular green alga *Haematococcus pluvialis* has been found to produce ethylene, although an enzymatic complex different from that present in higher plants was apparently used (Maillard *et al.*, 1993). *Acetabularia mediterranea* algae also produce ethylene, possibly by the same biosynthetic pathway as in higher plants (Kevers *et al.*, 1986).

Lichens with both eukaryotic and prokaryotic photobionts were found to naturally produce ethylene (Ott and Zwoch, 1992). Lichen samples (representing eight species) were obtained from south Sweden, the maritime Antarctic and western Germany. As with the unicellular alga, enzymes apparently different from those present in higher plants were involved in ethylene biosynthesis. Lurie and Garty (1991) concluded that the lichen *Ramalina duriaei* produces

ethylene using the same precursors as in plants, but with different enzymes. Even though ethylene biosynthesis and release occurs in a wide range of plants, algae and lichens, it appears there are differences in the mechanisms of production.

3.1.4 Animals and Humans

Mammalian production of ethylene is low, and has been observed in only a limited number of studies. Ram Chandra and Spencer (1963) observed a 3- to 4-fold increase in ethylene content of exhaled air from 3 non-smoking subjects relative to inhaled room air (7.9 $\mu g\ m^{-3}$). This was a very small, limited study. Ethylene in expired air was substantially higher from a smoker (120 $\mu g\ hr^{-1}$) than from a non-smoker (0.91 $\mu g\ hr^{-1}$) (Conkle *et al.*, 1975). There is insufficient data available with which to evaluate the contribution to the atmospheric pool from these natural sources; although, it is likely low relative to microbial and vegetative sources.

3.1.5 Other Natural Ethylene Sources

Ethylene is released into the atmosphere during volcanic activity (Stoiber *et al.*, 1971); however, annual global volcanic ethylene emissions have not been quantified. Smoke from forest fires also contains ethylene. Yokelson *et al.* (1999) measured ethylene over a forest wildfire and estimated the average ethylene mixing ratio at 46 $\mu g\ m^{-3}$. The amount of ethylene generated annually from fires of natural causes is unknown as ethylene production varies with the type and amount of vegetation burned. Generation of ethylene from fires of human origin is discussed below (Section 4.2.1, *Combustion*).

The rate of release of ethylene from the Atlantic Ocean was estimated to be 6×10^{-11} g $cm^{-2}\ h^{-1}$ (Rudolph and Ehhalt, 1981). Atmospheric removal was estimated at 9×10^{-11} g $cm^{-2}\ h^{-1}$. These estimates suggest that a concentration of 5.5 $\mu g\ l^{-1}$ ethylene is present in the north Atlantic (Rudolph and Ehhalt, 1981). In an earlier study, ethylene concentrations in the Gulf of Mexico, Caribbean Sea, Atlantic Ocean, and Pacific Ocean, were found to range from 0.5 to 8.3 $\mu g\ l^{-1}$ (Swinnerton and Lamontagne, 1974). The variation in concentrations among sample sites appeared to be a consequence of biological activity rather than environmental contamination.

Ethylene is produced biotically and abiotically in estuarine environments, with higher concentrations found in areas with high primary productivity (Lee and Baker, 1992). Ethylene concentrations in samples obtained from the Skidaway River (an estuarine river) near Savannah GA averaged 0.01 $\mu g\ l^{-1}$, which increased to 0.04 $\mu g\ l^{-1}$ following an 8-hour exposure to sunlight. Similar processes may occur in Alberta's aquatic systems; however, these are undocumented.

3.2 Anthropogenic Production of Ethylene

3.2.1 Combustion

Burning of agricultural field residues and forests contributes to atmospheric ethylene levels. While burning of agricultural wastes is becoming a less common practice, the ethylene level within the smoke from these fires is substantial. Combustion of wheat straw in a closed warehouse (a volume of 3,190 m^3) produced 0.2 g C_2H_4 kg^{-1} of straw (Gerakis *et al.*, 1978). Darley *et al.* (1966) reported that the combustion of wood chips generated 1.1 g kg^{-1}, while combustion of green brush resulted in the generation of 1.3 g kg^{-1} of brush burned, 1.1 g kg^{-1} of barley straw burned, and 0.4 g kg^{-1} of native (Californian) brush burned. Boubel *et al.* (1969) found that 0.8 g kg^{-1} was produced from grass and straw stubble burned under laboratory conditions. Levels of ethylene in the air were elevated near (10 m) the flame front of a burning wheat stubble field (total area 20,000 m^2); however, levels diminished rapidly such that 30 m from the flame front ethylene levels were not above pre-burn concentrations (Gerakis *et al.*, 1978). One hour after burning ceased, the level of ethylene in the air space of soil cracks was elevated (2,185 µg m^{-3}). This concentration is sufficient to affect plant root growth and development. Rapid diffusion and dilution of ethylene produced by burning stubble in smaller fields rapidly reduces air ethylene levels to background. Ambient levels would be expected to be higher in regions in which larger scale burning takes place.

Burning of agricultural wastes in Japan was investigated as a possible source of ground-level ethylene (Sawada, 1985). A concentration of 1.3 µg m^{-3} was observed at 1,200 m above ground level, increasing to 89 µg m^{-3} 1.2 m above the burning paddy fields. However, since the burning only occurs during a 4- to 5-day period in the afternoon and night in late October, Sawada (1985) suggested that these levels do not invoke significant responses by exposed plants.

Forest fires (both wildfires and managed burnings) also contribute to atmospheric ethylene levels. Sawada and Totsuka (1986) have estimated that burning of tropical rain forests is the single largest anthropogenic source of global atmospheric ethylene (20% of total anthropogenic emissions). Abeles (1982) suggested an average of 1 kg of ethylene is produced per tonne of burned vegetation in the United States. Yamate (e1974; cited in Abeles, 1982) estimated that the total contribution of ethylene from burning vegetation at 80 x 10^3 tonnes per year in the United States. More ethylene is released from burning vegetation during the smoldering phase (following peak fire activity). Application of flame retardant chemicals enhances ethylene emissions, possibly by lowering fire temperature and extending the length of the smoldering phase of the fire (Sandberg *et al.*, 1975). Smoldering wood, needles and litter produce more ethylene (up to 5 g kg^{-1}) than flaming wood, which produced less than 0.2 g kg^{-1} (McKenzie *et al.*, 1995). Estimates of ethylene emissions from burning in agricultural and forestry activities in Canada have not been made, and are considered to be very small relative to other sources (National Research Council of Canada, 1985). Since fires are essentially point sources of ethylene, and since diffusion and dilution rapidly reduce ethylene levels as the distance from the fire increases (Gerakis *et al.*, 1978), physiologically significant levels of ethylene are likely to occur only in areas near forest or agricultural fires (Abeles, 1982).

On an annual average basis (27-year average, from 1969 to 1995), approximately 85,000 ha of productive (capable of yielding 50 m^3 ha^{-1} of gross roundwood volume) and potentially productive (capable of producing a productive stand within 120 years) forests were burned per year in Alberta. Volume of wood lost (coniferous plus smallwood deciduous) averaged 2,846,000 m^3 per year, yielding an average loss of 33 m^3 ha^{-1}. Average annual ethylene emissions from these fires is estimated using the following assumptions: an average green weight of 600 kg m^{-3} for trees (pine, spruce, aspen), emissions of 1 g ethylene per kg of wood burned, and complete combustion. With these assumptions, it is estimated that 1,700 tonnes of ethylene per year is emitted into the atmosphere from forest fires in Alberta. Until actual measurements of ethylene emissions from Alberta forest fires are made, this value cannot be verified.

Jerman and Carpenter (1968) measured ethylene levels of up to 3% (by volume) in the smoke generated by municipal waste incineration. Up to 17,250 µg m^{-3} ethylene was detected in the flue gases of burned municipal waste in Babylon, NY; however, under good combustion conditions ethylene emissions were much lower (Carotti and Kaiser, 1972). The amount of ethylene generated depended upon the type of material burned and the water content of the waste. Municipal waste incineration does not contribute significantly to atmospheric ethylene levels in Alberta. Incinerators, such as the one in Wainwright, Alberta, and the one for hazardous waste in Swan Hills, Alberta, burn at temperatures that result in complete combustion of ethylene.

Ethylene levels in ambient urban air are primarily the result of vehicular activity (Nassar and Goldbach, 1979). Gasoline itself does not contain ethylene (Stephens and Burleson, 1967). Darley *et al.* (1966) estimated that 0.4% of the gasoline burned in an engine was released as ethylene. This value has likely changed with the modernization of gasoline engines and emission controls, along with developments in gasoline additives and technologies. Ethylene emissions from vehicular sources are presented in Table 3.1. Vehicular emissions contributed between 84 and 98% of the ethylene in urban air in the morning hours in downtown Los Angeles (Lonneman *et al.*, 1974). Emissions from vehicles at cold start-up did not differ from roadway emissions (warm vehicles) (Doskey *et al.*, 1992). In Porto Alegre, Brazil, where vehicle emissions represent 85.6% of total citywide hydrocarbon emissions, ethylene is the second most abundant hydrocarbon on a mass concentration basis (Grosjean *et al.*, 1998).

Recent regulations in several CO non-attainment areas of the United States required that oxygen content of gasoline be increased from to 1.8 to 2.7% by weight. Increased oxygenation results in reduced CO and total VOC emissions while NO_x emissions remain constant. Gasoline oxygenation also results in decreased ethylene emissions in proportion to the general reduction (18%) of VOC emissions (Kirchstetter *et al.*, 1996). Ethylene comprised 7.8% of the VOC emissions (by weight) from gasoline containing 0.3% oxygen (MTBE was the only oxygenate), and 7.2% (by weight) of the emissions from high oxygenate fuel (2.0% by weight; oxygenates were 80% MTBE, 20% ethanol). Gertler *et al.* (1996) reported similar values of 8.1 to 11.2% (by weight) of ethylene in the total VOC mass emitted from light-duty vehicles.

Other combustion processes (residential wood burning, office heating, tobacco smoking) produce ethylene. Emission factors for combustion processes that have been quantified are presented in Table 3.1.

Table 3.1 Ethylene emission factors for various anthropogenic combustion sources

Combustion Source	Ethylene Emission Factors	Reference
Residential wood combustion	1.13 kg tonne^{-1}	NRC (1985)†
Slash burning	0.15 kg tonne^{-1}	NRC (1985)
Wigwam burners	0.41 kg tonne^{-1}	NRC (1985)
Automobile (gasoline)	3.8 kg yr^{-1}	NRC (1985)
Light-duty trucks (gasoline)	4.4 kg yr^{-1}	NRC (1985)
Medium-duty trucks (gasoline)	9.3 kg yr^{-1}	NRC (1985)
Heavy-duty trucks (gasoline)	30.8 kg yr^{-1}	NRC (1985)
Agricultural equipment (gasoline)	1.9 kg·10^{-3} l^{-1}	NRC (1985)
Heavy-duty construction equipment (gasoline)	3.3 kg·10^{-3} l^{-1}	NRC (1985)
Industrial engines (gasoline)	3.2 kg·10^{-3} l^{-1}	NRC (1985)
Railway locomotives (diesel)	1.2 kg·10^{-3} l^{-1}	NRC (1985)
Heavy-duty trucks (diesel)	16.8 kg yr^{-1} veh^{-1}	NRC (1985)
Agricultural equipment (diesel)	0.8 kg·10^{-3} l^{-1}	NRC (1985)
Construction vehicles (diesel)	0.4 kg·10^{-3} l^{-1}	NRC (1985)
Other equipment (diesel)	0.5 kg·10^{-3} l^{-1}	NRC (1985)
Light-duty vehicles (measured in 2 tunnels):		Gertler *et al.* (1996)
Fort McHenry Tunnel (Baltimore MD)	43 mg veh-mile^{-1}	
Tuscarora Mountain Tunnel (PA)	27 mg veh-mile^{-1}	
Light-duty vehicles:		Sagebiel *et al.* (1996);
Fort McHenry Tunnel (Baltimore MD)	35.3 mg veh-mile^{-1}	Zielinska *et al.* (1996)
Tuscarora Mountain Tunnel (PA)	23.2 mg veh-mile^{-1}	
Composite of vehicle types:		Doskey *et al.* (1992)
Chicago IL Roadway	6.98 (wt%) of total NMHC	
Vehicle cold start	5.40 (wt%) of total NMHC	
Heavy-duty vehicles:		Sagebiel *et al.* (1996);
Fort McHenry Tunnel (Baltimore MD)	50.8 mg veh-mile^{-1}	Zielinska *et al.* (1996)
Tuscarora Mountain Tunnel (PA)	34.9 mg veh-mile^{-1}	
Diesel motors (2 makes, 11 heavy duty diesel fuels)	31.5 mg km^{-1} to 102 mg km^{-1}	Sjögren *et al.* (1996)

† NRC (1985) = National Research Council of Canada (1985)
†† veh-mile = vehicle-mile

3.2.2 Industrial Sources

Ethylene is used as a feedstock in a wide range of industrial processes leading to a diversity of end products (Kniel *et al.*, 1980; Considine and Considine, 1995), many of which are plastics. Therefore, petrochemical processing facilities that produce ethylene (by dehydrogenation of ethane), or use ethylene, are typical sources of anthropogenically-released ethylene.

At industrial facilities, ethylene may be released from stacks and flares, or as a result of leaks in pipe fittings (fugitive emissions). Environment Canada (1995, 2000) lists Alberta facilities that

reported ethylene releases (Table 3.2). Underground injections of ethylene are not included in Table 3.2, since these injections do not directly contribute to atmospheric ethylene levels. A total of 1,238.32 tonnes was released into the air in Alberta in 2000 from these industrial sources, up from 742.63 tonnes in 1995, 726.67 tonnes in 1994, and 561.86 tonnes in 1993 (Environment Canada, 1993, 1994, 1995, 2000). Alberta ethylene emissions increased from 31% (1995) to 46% (2000) of the total Canadian ethylene emissions (Environment Canada, 1995, 2000). Stack and fugitive emissions were the largest industrial sources of ethylene.

Flares at petrochemical facilities are designed to combust ethylene and other organic compounds in the event of facility upset. Flare emissions contain ethylene, and the amount of ethylene released depends upon the composition of the gas flowing to the flare (ethylene, methane, other hydrocarbons, condensate vapour, water, etc.), as well as the environmental conditions (especially wind) during flaring, and upon the extent of hydrocarbon combustion efficiency within the flare flame (Strosher, 1996). Ethylene is produced as a product of pyrolytic reactions within the flame (Strosher, 1996). The majority of ethylene generated within the flame is combusted in the outer combustion zone, but increased turbulence, or increased crosswinds, decreases combustion efficiency and under these conditions, ethylene emissions increase. This report is particularly relevant to Alberta given that more than $1,400 \times 10^6$ cubic meters of gas was flared in both 1999 and 2000 (Alberta Energy and Utilities Board, 2001). Emissions of ethylene from experimental laboratory and field flare systems, and operating sweet gas (no H_2S) and sour gas (H_2S present) flares are presented in Table 3.3. For the operating flares, approximately 8,000 m^3 per day was sent to flare at the sweet gas site, while 650 m^3 were sent to flare at the sour gas site; therefore, quantitative comparison of ethylene emissions from sweet and sour gas flares based on this work is not possible. This investigation represents the first time that VOC characterization and emissions from flares were determined; consequently, there is insufficient information to generalize flare emissions province-wide.

Based on the emissions presented in Table 3.3, and on calculated emission rates for the two operating flares, plume dispersion modelling was used to predict maximum ground level ethylene levels that might occur as a result of incomplete combustion within the flares (Strosher, 1996). On a daily average basis, a maximum of 0.5 $\mu g\ m^{-3}$ is predicted to occur within 3 km of the sweet gas flare. This is in addition to any ethylene already present in the ambient air (e.g. as a result of ethylene emissions from vegetation). On an annual average basis, flaring at this site is predicted to increase ethylene concentrations by 0.01 $\mu g\ m^{-3}$. Increases of 0.02 $\mu g\ m^{-3}$ (daily average) and 0 $\mu g\ m^{-3}$ (annual average) are expected to occur within 3 km of the sour gas site. It is important to recognize that this is the first study of this type, and that these results are specific to the two sites investigated. Emissions from other flares will vary depending upon the composition of the gas being flared, the size of the flare, environmental conditions at the time of flaring, and flare design.

3.2.3 Other Sources

Ethylene is released from activities in agriculture and forestry. These include emissions from stationary and field machinery, as presented in Table 3.1. Additionally, ethylene release from crops as a result of application of chemical compounds (herbicides, growth regulators) also contributes to elevated ethylene levels on a site-specific basis. The agricultural compound

Table 3.2 Ethylene releases (tonnes/year) from Alberta industrial facilities†

Facility	1995 Releases					2000 Releases				
	Stack	Storage	Fugitive	Other	Total	Stack	Storage	Fugitive	Other	Total
Union Carbide Ethylene Glycol Plant, Prentiss	227.83	0	0.33	0	228.15	270.60	0	2.66	0	273.26
Dow Chemical Canada Inc., Fort Saskatchewan	26.00	0.01	96.00	6.35	128.35	49.04	0.007	73.15	8.34	130.54
NOVA Chemicals, Research and Technology Centre	-	-	-	-	-	5.27	0	0	0	5.27
NOVA Chemicals, Joffre	46.00	1.60	97.00	0	144.60	245.71	0.24	59.23	0	305.18
Syncrude Canada Ltd., Fort McMurray	46.80	0	0.21	0	47.01	75.75	7.29	0.70	0	83.74
Celanese Canada Ltd., Edmonton	27.00	0	3.40	3.50	33.90	19.00	0	4.60	0.01	23.61
AT Plastics Inc., Edmonton	70.42	19.24	23.53	0	113.19	243.80	77.00	55.00	0	375.80
Imperial Oil Strathcona Refinery, Edmonton	3.15	0	19.40	0	22.55	0.84	0.03	8.77	0.07	9.71
Petro-Canada Refinery, Edmonton	0	0	7.40	0	7.40	0	0	0.66	0	0.66
Shell Canada Products Ltd., Styrene Monomer Manufacturing Plant, Fort Saskatchewan	0	0	0.48	0	0.48	14.39	0	4.34	0	18.73
Suncor	0	17.00	0	0	17.00	11.83	0	0	0	11.83
Totals	447.20	37.85	247.75	9.85	**742.63**	936.23	84.56	209.10	8.422	**1238.32**

† Data from Environment Canada National Pollutant Release Inventory

Table 3.3 Summary of ethylene emissions from experimental laboratory and field flares, and from two oilfield battery flares†

Experimental Flares Under Laboratory Conditions			
Flare Gas	**Combustion Conditions**	**Ethylene Detected within Flame**	**Ethylene Detected outside Flame**
Methane	Laminar Flow‡	1.25 g m^{-3}	—
Methane	Transitional¶	1.54 g m^{-3}	150 mg m^{-3}
Methane	Turbulent§	1.02 g m^{-3}	220 mg m^{-3}
Propane	Turbulent	1.56 g m^{-3}	180 mg m^{-3}
Natural Gas	Turbulent	1.10 g m^{-3}	160 mg m^{-3}
Methane + 15% Heptane			2.34 mg m^{-3}
Methane + 23% Heptane			1.64 mg m^{-3}
Methane + 32% Heptane			8.30 mg m^{-3}

Experimental Flares in Open Atmosphere with Calm Winds		
Flare Gas	**Combustion Conditions**	**Ethylene Detected 25 to 50 cm away from Flame**
Natural Gas	Turbulent	0.1 to 0.5 mg m^{-3}
Natural Gas + 15% Condensate Vapour	Turbulent	0.1 to 6.5 mg m^{-3}
Natural Gas + 23% Condensate Vapour	Cross Winds	0.1 to 0.6 mg m^{-3}

Operating Sweet and Sour Gas Battery Flares			
		Ethylene Detected	
Flare Gas	**1 to 2 m from Flame**	**4 to 5 m from Flame**	**8 to 9 m from Flame**
Sweet Solution Gas @ 1 to 2 m^3 min^{-1}	17 mg m^{-3}		
Sweet Solution Gas @ 5 to 6 m^3 min^{-1}		27 mg m^{-3}	9 mg m^{-3}
Sweet Solution Gas + liquid fuel + water	26 mg m^{-3}		
Sweet Solution Gas + liquid fuel	43 mg m^{-3}		
Sour Solution Gas	6 mg m^{-3}		

† Data from Strosher (1996).
‡ Laminar flow conditions were considered to be optimal for combustion (no turbulence or cross winds).
¶ Transitional flames contained significant flickering.
§ Turbulent conditions caused highly variable flames.

ethephon (2-chloroethylphosphonic acid) is used to modify plant growth and development. Ethephon decomposes to ethylene following incorporation into the plant. In Alberta, ethephon has been used to prevent lodging in cereal crops, the mode of action being primarily the reduction of stem elongation (Taylor *et al.*, 1991; Foster and Taylor, 1993). The ethylene diffuses out of the plant and into the atmosphere. Thus, applications of ethephon eventually contribute to atmospheric ethylene levels. At present, ethephon use in Alberta is limited.

4.0 ENVIRONMENTAL FATE AND BEHAVIOUR

Ethylene is naturally produced and metabolized by microorganisms, plants and animals. Additionally, ethylene is chemically reactive, and reactions that occur in ambient air remove ethylene from the atmosphere. Some of these reactions lead to the formation of ground-level ozone and photochemical smog.

4.1 Physical and Chemical Removal of Ethylene from Ambient Air

4.1.1 Chemical Removal of Ethylene

Ethylene is one of the more reactive VOCs and is oxidized in the atmosphere to form intermediate compounds (secondary pollutants), which will eventually break down to carbon dioxide and water. The global lifetime of ethylene in the troposphere is listed at 2.2 days (Warneck, 1988). However, there are literally hundreds of chemical reactions and photochemical cycles associated with the destruction of ethylene in the troposphere, ranging from several hours (Bufalini *et al.*, 1976; Simpson, 1995) to just a few (<7) days (Darnall *et al.*, 1976; Howard, 1976). The chemical mechanisms involved are complex and their rates dependent on the actual physical conditions as well as the presence of a large variety of potentially available reactants and intermediates. Only a few major representative routes will be discussed.

Although ethylene can be oxidized by species such as O_3 or NO_3, it is the hydroxyl radical (OH) which is central to the chemistry of ethylene in the troposphere. These radical-chain reaction processes in the troposphere are photochemically driven. The OH radical is primarily produced by the photochemical decomposition of ozone (O_3) by sunlight (equation 1) followed by hydrogen abstraction from water (equation 2).

(1) $$O_3 \xrightarrow[< 320\ nm]{sunlight} O_2 + O^*$$

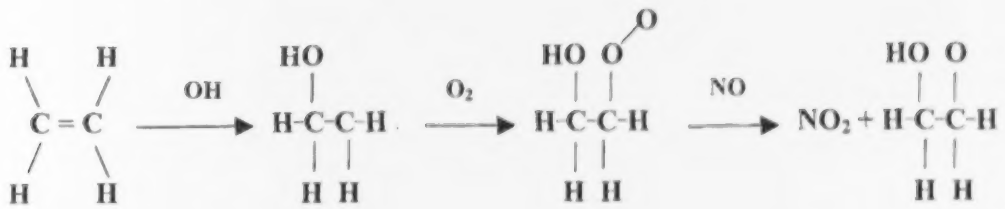
Ozone — oxygen

(2) $$O^* + H_2O \longrightarrow 2OH^*$$

hydroxyl radical

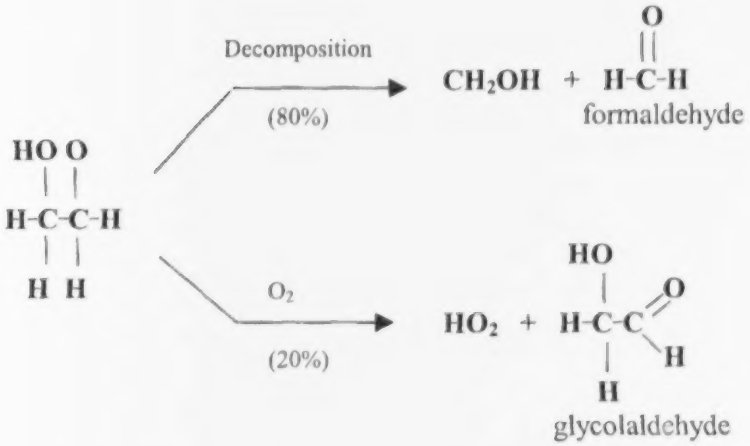
The resulting free OH radical is very reactive and can attack the double bond of the ethylene molecule (first step in equation 3). The reaction is fast with a rate constant of 8.52×10^{-12} $cm^3 \cdot molecule^{-1} \cdot second^{-1}$ (Atkinson, 1994), and with the reaction rate being dependent on OH concentration. For the average global OH concentration of 8.0×10^5 molecules $\cdot$ cm^{-3} (Prinn *et al.*, 1992) the half life of ethylene is about 27 hours. However, in more polluted urban areas where OH concentrations can reach 10^7 molecules $\cdot$ cm^{-3} (Eisele and Tanner, 1991) the half life is only about 2 hours. Through a series of subsequent chemical reactions ethylene can be transformed (equations 3 and 4) into other compounds (Finlayson-Pitts and Pitts, 1986).

(3)



ethylene

(4)



glycolaldehyde

The organic products generated (in equation 4) can be further degraded through similar reactions to produce carbon dioxide and water. Several of the intermediates, especially the peroxides, may adversely affect vegetation (Hatakeyama *et al.*, 1995; Hewitt and Kok, 1991). More importantly, the process of ethylene oxidation directly (equation 3) or indirectly (through HO_2 production in equation 4) generates NO_2, which can then lead to the formation of ozone (equations 5 and 6). Ozone is also phytotoxic (US Environmental Protection Agency, 1996).

(5) $$NO_2 \xrightarrow[< 400\ nM]{\text{sunlight}} NO + O$$

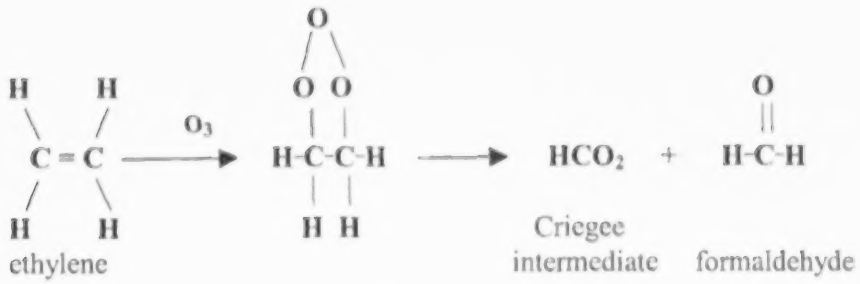
nitrogen dioxide — nitric oxide

(6) $$O + O_2 \longrightarrow O_3$$

oxygen — ozone

Ethylene has one of the highest photochemical ozone creation potentials of any hydrocarbon (Derwent *et al.*, 1996; Grosjean *et al.*, 1998), and based on environmental chamber experiments can produce 2.6 moles of ozone per mole of ethylene (Carter, 1995). This ozone can go on to produce more OH radicals (equations 1 and 2) or react directly with ethylene to form formaldehyde and the Criegee intermediate (equation 7), which both undergo further degradation (Niki *et al.*, 1983).

(7)



The rate of attack of ethylene by ozone is much slower than attack by the OH radical and is reflected in the substantially smaller ($k = 1.59 \times 10^{-18}$ $cm^3 \cdot molecule^{-1} \cdot second^{-1}$) rate constant (Atkinson, 1994).

Although oxidation by OH and ozone are the most important routes for ethylene removal in the daytime, oxidation by the nitrate radical (NO_3) dominates at night when there are no photochemical reactions (Wayne, 1991). The mechanism is thought to occur by nitrate addition across the double bond, which occurs slightly faster than attack by ozone. The rate constant ($k = 2.1 \times 10^{-16}$ $cm^3 \cdot molecule^{-1} \cdot second^{-1}$) is larger than for ozone attack, but much smaller than for the OH radical (Atkinson *et al.*, 1992).

The photochemical oxidation of ethylene throughout the troposphere is a natural process and is the same as the chemistry of photochemical smog. Thus, the principles of ethylene degradation occurring in rural environments are not different from the principles of urban ethylene degradation (Bunce, 1994). In urban environments where the volume of automobile traffic dramatically increases the presence of NO_x and hydrocarbons (including ethylene), ethylene oxidation is faster than in rural settings. However, while ethylene is reduced at a greater rate in urban environments, the photochemical reactions involved contribute to elevated levels of secondary pollutants and smog.

The complexity of both the large number of reactions and their interrelations has led to the extensive use of computer modelling to simulate conditions and species concentrations, as well as to evaluate reaction mechanisms (Simonaitis *et al.*, 1997; Carter, 1995). Carter (2000) described a mechanism that can be used in airshed models to represent the gas-phase atmospheric reactions of primary pollutants such as VOCs and NO_x to form secondary pollutants such as ozone. Carter's work (2000) updated the maximum incremental reactivity (MIR) and maximum ozone reactivity (MOR) scales. These scales quantify the amount of ozone formed with incremental increases in VOCs. While ethylene is not as reactive as many other hydrocarbons, use of this type of modelling could provide valuable information on ozone formation near ethylene emission sources.

4.1.2 Physical Removal of Ethylene

Removal of ethylene in the atmosphere can occur via gas scavenging by atmospheric water (e.g. cloud, rain, fog) followed by precipitation to the Earth's surface. This wet deposition is

proportional to the washout ratio (W_g) and varies with the Henry's Law constant (K_H) of ethylene:

$$W_g = [\text{ethylene}]_{rain} / [\text{ethylene}]_{air} = RT / K_H = RTC_w / P$$

where R is the ideal gas constant, T is the ambient temperature, P is the partial pressure and C_w is the aqueous solubility (Bidleman, 1988). This mechanism of wet deposition is an efficient process for removing atmospheric gasses possessing a large W_g value (i.e. high aqueous solubility) and a long atmospheric lifetime (> 10 days). The W_g values for VOCs such as methane (0.035), ethane (0.050), or ethylene (0.128) are much lower than gasses like SO_2 (42.4) that can readily undergo vapour scavenging. These values were computed from gas solubilities (at 20°C) listed in Dean (1985). In addition, the chemical breakdown of ethylene is relatively fast giving a global atmospheric lifetime of 2.2 days. This combination of low aqueous solubility and short atmospheric lifetime make removal of ethylene by wet deposition of minor or negligible importance (Atkinson, 1995).

4.2 Biological Removal of Ethylene from Ambient Air

Soil bacteria and fungi both remove ethylene from the air spaces within the soil. The amount removed is dependent upon abiotic (temperature, soil moisture, oxygenation level) and biotic factors (number of species present). The ability of a soil to act as a sink varies among ecosystems, with agricultural soils (cropping, forage production) and forest soils differing in their ethylene-removal capabilities. Initial investigations suggested that the soil might act as sink for atmospheric ethylene (Abeles *et al.*, 1971). However, sorption by a variety of soils as a result of microbial activity was found to be minimal (Smith *et al.*, 1973). The extent of ethylene removal from the atmosphere by the soil was investigated by Sawada *et al.* (1986) using a model that incorporates rates of diffusion into the soil and degradation within the soil. The model predicted that the soil would not act as a large sink for atmospheric ethylene, even in polluted atmospheres. Chemical reactions in the atmosphere were found to be 30 to 60 times more effective in removing ethylene from the air than was degradation within the soil. This investigation was conducted using the soil gathered from a Japanese cedar (*Cryptomeria japonica*) forest; it is likely that soils from other ecosystems would behave differently. Never the less, it is unlikely that ethylene removal by any soil would approach the chemical reaction and removal rates that occur in the atmosphere.

There is some evidence that ethylene is bound within soils as a result of non-biological processes. It is likely, that ethylene sorbed by soils in this fashion would either be re-released into the atmosphere, or eventually degraded by soil biota. As this is a slow process, degradation of ethylene by soil biota is unlikely to be a major ethylene removal process.

In order to act as a plant hormone, exogenous (atmospheric) ethylene must be incorporated into the plant. Recognition of an ethylene signal may result in metabolism of the incorporated ethylene. Plants can metabolise ethylene to form ethylene oxide and ethylene glycol (Beyer, 1984; Dodds *et al.*, 1979), but the amounts removed from the atmosphere by this process appear to be small.

5.0 MEASUREMENT AND MONITORING OF ETHYLENE

5.1 Collection of Samples

The proper choice of a sample container is important in obtaining an accurate measurement of ethylene concentration in air. Air samples are often collected in bags, syringes or other containers, and transported to a laboratory for analysis. Regardless of the container chosen, the system of sample collection and transport must be carefully checked to ensure that there is no ethylene loss (leakage, decomposition, adsorption to the container), or generation of ethylene as a result of chemical reactions within the container. If the sample containers are to be reused, it is equally important to ensure that the containers do not have an "ethylene memory" (release of ethylene adsorbed onto the inner lining into subsequently collected samples).

5.1.1 Sample Bags

Sample bags are available commercially, and have been used successfully (Sawada, 1985). Sample bags composed of aluminum foil sandwiched between polythene (inside) and polyester (outside), and of aluminum foil between polyester (inside and outside) have been successfully used to transport samples collected in the field to the laboratory (Rymen, 1979). However, the bags must be checked under the conditions in which they are to be used to ensure that they do not introduce artifacts into the sample. Either ethylene, or a contaminant chromatographically similar to ethylene, was found to be emitted from Teflon coating of sample containers used in aircraft sample collection systems (Rasmussen and Robinson, 1977; cited in Robinson, 1978). As a result, ethylene could not be quantified in these samples. Seila *et al.* (1976) found compounds with retention times similar to ethylene, propylene, acetylene, butene, 1-pentene, toluene, acetone and acetaldehyde as contaminants originating from Tedlar (polyvinylfluoride) bags exposed to light (wavelength of 310 to 390 nm). Irradiation also irreversibly altered the storage potential of these bags. If these bags are stored carefully (prevention of bag exposure to light), they can be used for ambient air storage prior to analysis.

Losses of 16% to 26% of organic compounds (toluene, trichloroethylene, and 1,2-dichloroethane) occurred during the first 24 hours of sample storage in commercial Tedlar bags (Wang *et al.*, 1996). Modification of the bags by replacing the hose valve with a septum reduced losses to 8% to 13% during the first 24 hours of sample storage. Losses from sample bags constructed by Wang *et al.* (1996) from bulk Tedlar film and Teflon valves were in the range of 4% to 11%. Wang *et al.* (1996) concluded that it was the hardware supplied with the sample bags, not the bag material itself, which was the cause of losses. Although ethylene loss from these bags was not investigated, leakage from the bags would not be chemical-specific. Thus, if sample bags are to be used for ethylene sampling, they must be tested prior to use to ensure that sample loss from the bag does not occur.

5.1.2 Syringes

Blankenship and Hammett (1987) quantified loss of ethylene from plastic and glass syringes. Ethylene losses approached 50% after 30 hours storage of a plastic syringe initially containing 11,500 $\mu g\ m^{-3}$ ethylene. Both, diffusion out of the syringe and adsorption of ethylene to the syringe wall contributed to the loss. Loss from glass syringes was smaller, approaching 25% after storage of 11,500 $\mu g\ m^{-3}$ ethylene for 30 hours.

5.1.3 Glass and Metal Containers

Air samples were successfully collected and analyzed for ethylene (as well as a number of other non-methane hydrocarbons) in Sydney, Australia (Nelson and Quigley, 1982) using an active sampling system. Air was sucked through Teflon tubing into 400-ml glass pipettes that were connected in series, and following a time sufficient to completely purge the system the pipettes were sealed by closing the attached Teflon valves. Pipettes were stored in the dark and transported to the laboratory for analysis. By sucking the air through the pipettes, rather than by pushing the air with the use of a pump, the need for a Teflon-coated pump was removed.

Evacuated stainless steel containers (2 litre) were used for sampling of air (Rudolph *et al.*, 1981). A rigorous cleaning and pretreatment regime was used to eliminate the possibility of cross-contamination of samples ("ethylene memory"). Samples were stored for as long as 3 months without detectable sample degradation. Brymer *et al.* (1996) determined that ethylene was not degraded, nor produced, within SUMMA polished canisters (stainless steel vessels treated to expose a smooth nickel and chromium oxide surface) during a 30-day sample storage period. The use of SUMMA containers for sampling of air for VOC analysis is now an established and accepted technique (Environmental Protection Agency, 1988), and these containers are currently being used in Alberta for VOC sample collection (Cheng *et al.*, 1997).

5.1.4 Mercuric Perchlorate

Air samples may be bubbled through a solution of mercuric perchlorate ($HgClO_4$), an ethylene trap (Abeles, 1973; Abeles *et al.*, 1992). In the laboratory, the trapped ethylene is released into the container headspace by addition of lithium chloride, and a subsample of the headspace is analyzed for ethylene. Absorption of ethylene into $HgClO_4$ minimizes ethylene losses during transport to the laboratory; however, $HgClO_4$ has the disadvantages of being corrosive, explosive and poisonous. Evidence of incomplete trapping, and incomplete release of ethylene from solution, has been presented (De Greef *et al.*, 1976). For these reasons, this method is seldom used.

5.2 Measurement of Ethylene

Chromatographic separation of ethylene from other compounds present in an air sample, followed by detection and quantification using a flame-ionization detector (FID) is the most common method of ethylene measurement. A diversity of chromatographic materials are available, and there is no one material which is preferred for ethylene purification and analysis. FID detectors have limitations, such as low selectivity and sensitivity (Singh & Zimmerman, 1992), some of which may be overcome by modification of the chromatographic system, or by use of a different detector such as mass selective or photo-ionization detectors. The choice of detector will depend upon the concentrations to be analyzed. Some of the methods with low detection limits are presented in Table 5.1; these are discussed in detail below.

Table 5.1 Selected analytical methods with low detection limits for the purification and quantification of ethylene in air

Pretreatment	Purification System	Volume (ml)	Detector and Detection Limit ($\mu g\ m^{-3}$)	Reference
Concentration in a multisorbent (3 media) precolumn at -185°C and ambient temps.	DB-1 capillary column (60 m x 5 µm I.D.). Isothermal operation.	285	FID[¶] 0.22	Oliver *et al.* (1996)
Cryogenic trap (freeze-out tube) at -189°C.	GS-Alumina column (30 m x 0.53 mm I.D.). 4-stage temp. program.	400	FID 0.01	Goldstein *et al.* (1995)
Cryogenic trap (column of glass beads) at -189°C.	Stainless steel Durapak n-octane/Porasil C column (6 m x 3 mm O.D.)	200	FID 0.5	Colbeck and Harrison (1985)
Concentration in a multisorbent (2 media) precolumn at -35°C.	Spherosil X0B 075 packed column (7 m x 0.8 mm I.D.).	1,000	FID 0.008	Rudolph *et al.* (1981)
None	Porapak Q or Porapak N, packed column	5	FID 5.8	Nassar and Goldbach (1979)
Cryogenic trap (column of glass beads) at -189°C.	Durapak octane/Porasil C column (6.1 m x 1.5 mm O.D.). 3-stage temp. program.	400	MS 0.1[†]	Nelson and Quigley (1982)
Continuous flow-through system.	CO_2 laser tuned to ethylene (non-chromatographic system)	900 ml hr^{-1}	Photoaccoustic cell[‡] 0.007	Voesenek *et al.* (1990)
Continuous flow-through system.	CO_2 laser tuned to ethylene (non-chromatographic system)	900 ml hr^{-1}	Photoaccoustic cell 0.023	Harren *et al.* (1990)

¶ Abbreviations: FID, flame-ionization detector; MS, mass spectrographic detector.

† Indicates the lowest ethylene concentration measured, not necessarily the detection limit.

‡ The CO_2 laser coupled with a photoaccoustic cell is not a chromatographic system, however these methods are presented here for comparison.

5.2.1 Chromatographic Purification and Analysis of Ethylene

Several detectors for gas chromatographic quantitation of ethylene are available. The thermal conductivity detector (TCD) is particularly insensitive; ethylene can not be detected at the mg m^{-3} (e.g. 1,000 μg m^{-3}) level with this detector (Lamb *et al.*, 1973). The flame-ionization detector (FID) is the most common detector used, having a lower detection limit of about 12 μg m^{-3} in a 5 ml sample (Abeles *et al.*, 1992). The amount of sample that can be directly injected onto a chromatograph is generally limited to 5 ml, as larger volumes will extinguish the detector flame. Because the concentration of ethylene in ambient air is generally low, analysis of large air samples may be necessary in order to obtain reliable results. Injecting larger volumes onto a precolumn that traps the ethylene and releases most of the other gases to the atmosphere, overcomes many of the problems associated with the measurement of low ethylene concentrations. The traps are made out of tubing (usually stainless steel) packed with molecular sieves (Harbourne *et al.*, 1973). The molecular sieves can be packed with chromatographic media, such as one of the Poropak materials (De Greef *et al.*, 1976; Galliard and Grey, 1969; Reid and Watson, 1981; Sawada, 1982; Stephens and Burleson, 1969) or dimethyl sulfolane-coated supports (Stephens and Burleson, 1967). In either case, the sample is injected slowly onto the trap, which is kept cold (5°C for molecular sieve, -80°C for Poropak and dimethyl sulfolane materials), and is open to atmosphere on the downstream side of the media. The trap is then closed to atmosphere, heated, and opened to the analytical chromatographic column. The gas chromatograph carrier gas sweeps the ethylene into the analytical system. Use of a precolumn (1 to 1.3 g of 13X molecular sieve in a 180 mm long section of ¼" I.D. stainless tubing) to preconcentrate ethylene lowered the detection limit to 2 μg m^{-3}, based on an injection of a 1 litre air sample (Harbourne *et al.*, 1973). Stephens and Burleson (1967), used a dimethyl sulfolane column and cold-trapping to reduce the detection limit to 1 μg m^{-3} ethylene in 100 to 500 ml air samples. While cold trapping is used primarily for preconcentration of ethylene from large gas samples, it also helps to purify ethylene and remove compounds that interfere with the ethylene analysis (Galliard and Grey, 1969).

In some cases it may be necessary to remove moisture from the sample prior to injection onto the cold column; this can be accomplished by passing the sample through a potassium carbonate drying tube prior to injection onto the precolumn (Westberg *et al.*, 1974). Other water removal materials (silica gel, molecular sieve) removed the water but interfered with ethylene analysis.

An automated system has been developed for sampling and GC analysis of ozone precursor concentrations in ambient air (Oliver *et al.*, 1996). This system includes an automated sampler that collects air over a 57-minute period at 5 cm^3 min^{-1}, and passes this air through an organic vapour concentrator coupled with a cryo-focussing trap. This two-trap system, allows the collection of a sample on one trap while the other is being purged. A total of 285 cm^3 are thus sampled. At the end of the 57-minute collection period, the trap is purged with dry helium to remove water (which interferes with the chromatography), and the trapped compounds are desorbed at 230°C and swept onto a GC column. For ethylene, cryo-cooling of the trap (-185°C) was found to be unnecessary, as effective trapping of ethylene occurred at ambient temperatures. This makes the system much more useful for field use. The ethylene detection limit using this system was found to be 0.22 μg m^{-3}. Analysis of a sample containing low concentrations of

ethylene and acetylene (at or below 12 μg m^{-3}) was not possible, since the two compounds were not resolved thus rendering quantitation impossible. It is also important to note that the data generated by this system essentially represents a one-hour average ethylene concentration due to the sampling of air over a 57-minute period.

An automated system that allows *in-situ* (unattended) sampling and analysis, with an ethylene detection limit of about 0.01 μg m^{-3}, has been described by Goldstein *et al.* (1995). Components of this system include a cryo-cooled preconcentrator and a gas chromatograph equipped with a FID. Ethylene recovery and elution from the cryo-cooled column were consistent and near 100%.

Use of Durapak *n*-octane/Porasil C as an analytical column packing, a sub-ambient temperature program, and a GC equipped with an FID, allowed detection of ethylene as low as 0.6 μg m^{-3} (Colbeck and Harrison, 1985). Rudolph *et al.* (1981) lowered the ethylene detection limit to 0.008 μg m^{-3} by trapping the C_2 to C_5 hydrocarbons (500 to 1000 ml sample) on a stainless steel precolumn (12 cm x 1/8 inch I.D.) containing 5 cm of porous silica and 5 cm Carbosieve B (column temperature of -35°C). Followed by analysis on a 7 m x 0.8 mm I.D. packed column containing Spherosil X0B 075 packing.

Photoionization detectors (PID) that utilize a lamp that emits light in the UV range (120 nm) are more sensitive to ethylene than are FIDs. Detection limits are in the region of 0.1 to 0.5 μg m^{-3} in a 1 ml sample. Generally, smaller samples may be analyzed (maximum injection volume is usually 1 ml), and cold trapping isn't required. Chromatographs equipped with a PID may be portable, facilitating field use. PID technology is advancing rapidly, and improved chromatographic systems using PID are now entering the market. While there is no published information regarding absolute detection limits for ethylene, it is recognized that these systems are more sensitive than FID, and are more amenable for use outside of the laboratory.

Measurement of ozone levels based on the reaction of ozone with ethylene is a common technique (e.g. Perkins *et al.*, 1993), but the reverse is also possible. Mohan Rao *et al.* (1983) used chemiluminescence to measure ethylene. The limit of detection by direct injection of 10 ml was 115 μg m^{-3} ethylene; however, by adding a cold-trap precolumn to the GC system, the detection limit was reduced to a 1 to 10 μg m^{-3} range (actual limit not given).

Sexton and Westberg (1984) attempted to measure ozone levels and sample for ethylene at the same site. The use of ethylene as a reactant in the chemiluminescent ozone monitor resulted in contamination of the air samples subsequently analyzed for ethylene. Contamination of air samples from hydrocarbon sample bags located near ozone monitors was also reported by Arnts and Meeks (1981). They emphasized the importance of proper location selection and methodology when investigating hydrocarbon content of ambient air.

5.2.2 *Laser Detection and Remote Sensing Systems*

Harren *et al.* (1990) used a CO_2 laser coupled to a photoaccoustic detector to measure low concentrations of ethylene in air. The reported detection limit of this system was 0.023 $\mu g\ m^{-3}$, allowing the detection and measurement of ethylene released from a single orchid flower. Voesenek *et al.* (1990) used this system to monitor ethylene release from a single waterlogged plant of *Rumex* spp. (whole plant). The detection limits reported (0.007 and 0.023 $\mu g\ m^{-3}$) are low, and ethylene levels between 0.6 and 1.2 $\mu g\ m^{-3}$ were accurately detected. While the laser photoaccoustic system is very sensitive to ethylene, it is very expensive and delicate, making it difficult to build and operate in the field for routine monitoring.

Menzies and Shumate (1976) used a bistatic laser system to monitor ethylene levels across a highway in the Pasadena CA area. Absorbance of several known wavelengths of CO_2 laser light across an atmospheric path provided the basis for ethylene quantification. The detection limit was not given. Although this technique has not been used routinely, possibly due to the expense and difficulty of use of the laser apparatus relative to gas chromatographic techniques, it is an emerging technique with much promise.

Yokelson *et al.* (1999) utilized airborne Fourier Transform Infrared spectroscopy (FTIR) to measure trace gases at various altitudes above biomas fires. Ethylene measurements ranged from 22 to 156 $\mu g\ m^{-3}$. The Institute for Research in Construction (IRC) utilizes Fourier Transform Infrared spectroscopy to assess combustion by-products. The IRC (2000) indicates the FTIR spectrometric technique has definite advantages over previous methods as it can provide continuous monitoring of secondary gases such as ethylene.

5.3 Quality Assurance and Quality Control (QA/QC) Protocols

In any survey of ethylene levels in ambient air, a Quality Assurance/Quality Control protocol is required. The QA/QC protocol, and subsequent validation of the data, for the Southern Oxidants Study 1992 Atlanta Intensive monitoring program provides a good review of the need for QA/QC, as well as a protocol for a QA/QC program (Apel *et al.*, 1995; Bernardo-Bricker *et al.*, 1995). Several laboratories were involved in the analysis of ambient air samples. In addition to the experimental samples, each laboratory was supplied with a series of standards that were analyzed each day to ensure correct instrument calibration and to verify retention time windows for identification of the target compounds (one of which was ethylene). A QA/QC protocol is necessary for programs that use more than one instrument or facility for the measurement of ethylene in ambient air. In programs in which a single instrument is used, proper calibration is required at regular intervals (daily at a minimum). Alberta Environment and Alberta Sustainable Resource Development have implemented a Laboratory Data Quality Assurance Policy to ensure analytical data and data from different sources are reliable, of consistent quality, and consistent with national and international standards.

5.4 Monitoring Fugitive Emissions of Ethylene

Fugitive emissions from petrochemical facilities are a significant anthropogenic source of ethylene in areas adjacent to the facilities (Table 3.2). Measurement of such emissions is difficult, due to the diversity and number of individual sources. In Canada, all industries producing or using volatile organic compound (VOC) streams must follow the Canadian Council of Ministers of the Environment (1993) *Environmental Code of Practice for the Measurement and Control of Fugitive VOC Emissions from Equipment Leaks*. Monitoring of ambient ethylene around such facilities gives an indication of the total release of ethylene, including that portion due to fugitive emission. Monitoring also provides information on exceedences, if any, of objectives and allows owners to implement measures to prevent such exceedences. Table 5.2 provides ambient ethylene monitoring data for 1999 to 2001 for three petrochemical sites in Alberta.

Monitoring and modelling of fugitive emissions may also be accomplished through the use of tracer gases. Tracer gases (SF_6 and $CBrF_3$) were released near fittings suspected of releasing ethylene in amounts proportional to the suspected leakage of ethylene, and were monitored downwind of the facility (Siversten, 1983). Application of Gaussian models to the SF_6 data accurately predicted the ethylene concentration downwind of the facilities (Siversten, 1983). Recently, many petrochemical facilities in Alberta have used dispersion models to estimate ethylene concentrations near the facilities arising due to fugitive emissions from the plant sites.

Table 5.2 Ambient ethylene monitoring data for three Alberta petrochemical facilities

	Facility 1		Facility 2			Facility 3	
Date	Monitoring station 1	Monitoring station 2	Monitoring station 1	Monitoring station 2	Monitoring station 3	Monitoring station 1	Monitoring station 2
1999							
May	-	-	51.59	42.42	-	58.47	8.03
June	-	-	42.42	29.81	-	30.96	4.59
July	-	-	38.98	25.22	-	47.58	8.03
Aug	-	-	27.52	22.93	-	48.15	6.88
Sept	-	-	83.69	42.42	-	20.64	12.61
2000							
May	-	-	16.05	14.90	37.83	3.44	3.44
June	35.54	61.91	18.34	28.66	22.93	10.32	3.44
July	127.26	42.42	20.64	10.32	28.66	67.64	4.59
Aug	65.35	11.46	20.64	26.37	41.27	5.73	2.29
Sept	198.34	104.33	58.47	49.30	81.40	232.74	11.46
2001							
May	-	-	16.05	98.60	6.88	26.37	4.59
June	-	-	37.83	29.81	99.74	28.66	6.88
July	-	-	16.05	77.96	13.76	64.20	9.17
Aug	-	-	-	-	-	36.69	32.10
Sept	-	-	-	-	-	45.86	20.64

Values shown are the maximum 6 hour average in $\mu g\ m^{-3}$ for the indicated month. A dash indicates the data was not available.

5.5 Acetylene as a Marker of Ethylene Emissions from Automobiles

Atmospheric acetylene (C_2H_2) is almost exclusively produced by vehicular activity, and acetylene was thought to be resistant to photochemical degradation (Stephens and Burleson, 1967, 1969). Therefore, acetylene has been used as a marker of automobile emissions (Stephens and Burleson, 1967, 1969; Warneck, 1988). In unreacted ambient air in Riverside CA, the ratio of ethylene to acetylene was found to be 0.81, similar to that found in other urban areas (Stephens and Burleson, 1969). However, Kopczynski *et al.* (1975) found that unknown, but very effective removal processes might reduce atmospheric acetylene levels. Therefore, use of acetylene as a marker of automobile emissions was suspect. Whitby and Altwicker (1978) suggest that ambient air acetylene levels and ratios with other hydrocarbons do provide useful and generally accurate tools in air pollution studies. Greater knowledge of industrial and natural acetylene emissions and environmental reactions is required before the use of ethylene to acetylene ratios can be used as a quantitative tool in the estimation of automotive emissions (Whitby and Altwicker, 1978).

6.0 AMBIENT LEVELS

6.1 Remote and Rural Environments

Ethylene concentrations measured in rural and remote environments are summarized in Table 6.1. Levels in these locations are generally below 15 μg m^{-3}; these levels are considered to represent local background ethylene levels.

Table 6.1 Ethylene levels in ambient air in rural and remote locations

Location, Date, Time of Day	Ethylene (μg m^{-3})	Reference
Above and below boundary layer in both N. and S. latitudes. Jun. 1978	0.2	Rasmussen and Khalil (1982)
Boundary layers from 300 to 1200 m above sea level, Japan	0.6 to 1.3	Sawada (1985)
Subalpine coniferous forest, NW of Calgary AB, Aug. to Sept. 1981	3 to 14	Reid and Watson (1981)
Rural MO, Dec. 1972, 0800 to 0900 hr	4	Kopczynski *et al.* (1975)
Rural FL, 1000 to 1900 hr, May 18, 1976	2 to 4	Lonneman *et al.* (1978)
Rural OK, Jul. 27, 1978	<1	Arnts and Meeks (1981)
Rural ME, CA, WI, TX, IL, Summer 1975 to 1978	2 (max)	Sexton and Westberg (1984)
Elkton MO, 1975	4 (max)	Robinson (1978)
Louisiana, Dry and Swamp Forests, June 1990	0.4 to 0.5	Khalil and Rasmussen (1992)
50 km upwind of Mexico city (Pyramid of the Moon) 1230 hr, Feb. 21, 1993	0.7	Blake and Rowland (1995)
Rural NW England, Feb. to Mar. 1978	<14	Harrison and Holman (1980)
Rural NW England, summer 1983	2	Colbeck and Harrison (1985)
Pallas, Finland (high elevation)		Laurila and Hakola (1996)
Jan. 1993/4	0.6	
Jul. 1993/4	0.05	
Uto, Finland (Baltic Sea island)		
Dec. 1993/4	1.0	
Jun. 1993/4	0.1	
Japan, fall 1980/1		Sawada (1985)
300 to 1200 m above sea level	0.6 to 1.3	
Fagus crenata forest	3 to 15	

Cavanagh *et al.* (1969) attempted measurements of ethylene levels at Point Barrow, Alaska. Ethylene and ethane did not completely separate in their chromatographic system, nor did they calibrate the instrument using standard ethylene (other compounds were used to calculate FID response). The concentration of the composite ethylene-ethane component did not exceed 0.09 μg m^{-3}. The only conclusion possible from this work is the qualitative statement that background ethylene levels in Alaska are expected to be quite low.

Atmospheric ethylene concentrations in and above the boundary layer in both northern and southern latitudes were relatively constant, averaging approximately 0.2 μg m^{-3} (Rasmussen and

Khalil, 1982). Levels between 0.6 and 1.3 μg m^{-3} were measured in samples collected above Japan from between 300 and 2,000 m above sea level (Sawada, 1985). Analysis of wind patterns and velocity suggested that anthropogenic sources did not contribute to these levels. Saito *et al.* (2000) measured ethylene levels of 0.13 to 1.77 μg m^{-3} at sea level, in the western North Pacific and the eastern Indian Ocean. After back trajectory analysis of air movement, it was concluded that ethylene was derived from either continental (26°S samples) or oceanic (25°N samples) sources (Saito *et al.*, 2000).

Measurements of ethylene levels in a subalpine coniferous forest northwest of the City of Calgary showed a cyclical pattern of ethylene levels, with the highest concentrations occurring at 1300 hr (14 μg m^{-3}) and the lowest at 2100 hr (3 μg m^{-3}) (Reid and Watson, 1981). This cycle was attributed to ethylene produced by vegetation during the daylight hours. These measurements indicate that a summertime (late June) background level of ethylene in Alberta is in the range of 2 to 14 μg m^{-3}.

Emissions from soft and hard wood tree species in both dry and swamp environments in Louisiana generated ambient ethylene levels between 0.4 and 0.5 μg m^{-3} (Khalil and Rasmussen, 1992). These levels are an order of magnitude lower than levels observed in Alberta forest environments (Reid and Watson, 1981).

6.2 Urban Environments

Ethylene concentrations in urban and suburban environments are summarized in Table 6.2. Observed levels vary from 4 μg m^{-3} in downtown Tulsa OK (Arnts and Meeks, 1981) to a high of 805 μg m^{-3} found in downtown Washington DC (Abeles and Heggestad, 1973). From 1984 to 1985 the median concentration of ethylene in 39 US cities was 12.3 μg m^{-3} (Seila et al., 1989). Since automobile exhaust contains high levels (282,900 μg m^{-3}) of ethylene (Neligan *et al.*, 1961), automobiles are the major sources of urban ethylene.

Concentrations between 40 and 69 μg m^{-3} were found in the eastern industrial areas of Calgary, and further to the east of this development (Reid and Watson, 1981). Ethylene concentrations decreased as distance from the city increased. Within the city, a maximum of 113 μg m^{-3} was reported during a winter temperature inversion. These inversions are known for trapping pollution at or near ground level, and for preventing wind at ground level. Levels between 14 to 69 μg m^{-3} were generally found in the city or downwind of the downtown core. Recent monitoring data indicates the ethylene concentration in downtown Calgary averaged 7.46 μg m^{-3} (Table 6.3), (Clean Air Strategic Allicance, 2002).

The median ethylene concentration in downtown Edmonton, during the period of December 1991 through November 1993 was 4.99 μg m^{-3}, based on samples collected over a 24- hour period, every sixth day (Cheng, *et al.*, 1997). More recent monitoring data indicates the average ethylene concentration in Edmonton east was 4.31 μg m^{-3}, and 7.28 μg m^{-3} in Edmonton central, (Table 6.3), (Clean Air Strategic Alliance, 2002).

Table 6.2 Ethylene levels in ambient air in urban and suburban environments

Location, Date, Time of Day	Ethylene ($\mu g\ m^{-3}$)	Reference
Calgary AB		Reid and Watson (1981)
Roadside 1981	12 to 24	
U. of Calgary, Feb. to May 1981	14 to 33	
U. of Calgary, Jan. 27 1981(temperature inversion)	113	
Eastern (downwind) side, Feb. and May 1981	40 to 69	
Edmonton AB, Dec. 1991 to Nov. 1993		Cheng *et al.* (1997)
Downtown	4.99	
East-side Industrial Area	4.53	
Sarnia ON, 1978 to 1983, average annual	6 to 14	Lambdon Industrial Society (1983)
California		
Los Angeles, 0700 to 0800 hr, fall 1967	89	Altshuller *et al.* (1971)
Los Angeles, 1200 to 1300 hr, fall 1967	29	Altshuller *et al.* (1971)
Azusa, 0700 to 1300 hr, fall 1967	21 to 24	Altshuller *et al.* (1971)
Azusa, 0500 to 1600 hr, fall 1967	9 to 21	Gordon *et al.* (1968)
Riverside, 0815 hr, Jan. 23, 1968	144	Stephens and Burleson (1969)
Pasadena CA, Freeway 1000 to 1200 hr	9	Menzies and Shumate (1976)
Pasadena CA, Freeway 1600 hr	39	Menzies and Shumate (1976)
St. Louis MO, 0800 to 0900 hr, Dec. 1972	39	Kopczynski *et al.*, 1975
Downtown Miami FL, 0800 hr, May 18, 1976	12	Lonneman *et al.*, 1978
Tulsa OK, Downtown 0953 to 1053 hr, Jul. 27, 1978	4	Arnts and Meeks (1981)
Tulsa OK, Suburban 0825 to 0925 hr, Jul. 27, 1978	5 to 7	
Washington DC Downtown, summer day 1972	805	Abeles and Heggestad (1973)
Washington DC Suburban, summer day 1972	45	
Metropolitan Denver CO, 0800 to 1200, Oct. 1971 to Feb. 1972	207 (max)	Hanan (1973)
Philadelphia PA, Suburban	6 to 117	Giannovario *et al.* (1976)
Mexico City, Mexico		Blake and Rowland (1995)
Downtown (Zocalo), 0600 hr, Feb. 21, 1993	18	
Downtown (Zocalo), 1200 hr, Feb. 18, 1993	32	
Tlalpan Highway, 1645 hr, Feb. 20. 1993	193	
Sydney, Australia, morning Sept. 1979 to Jun. 1980	14	Nelson and Quigley (1982)
Hamburg, Germany, 0900 to 1100 and 1600 to 1900, summer 1976, high traffic area	173 (max)	Nassar and Goldbach (1979)
Hamburg, Germany, 0900 to 1100 and 1600 to 1900, summer 1976, low traffic area	58 (max)	
Hamburg, Germany, night, summer 1976	12 to 23	
Minden, Germany, late night, summer 1976	6	
Delft, The Netherlands	18	Bos *et al.* (1977)
Urban Swansea, South Wales (early 1970's)	322	Harbourne *et al.* (1973)
Semi-rural Swansea, South Wales (early 1970's)	230	
Urban NW England, summer 1983	49	Colbeck and Harrison (1985)
"Polluted" Rural England, summer 1983	26	
NW England, populated areas, Feb. to Mar. 1978	<9	Harrison and Holman (1980)

Table 6.3 Ethylene levels in ambient air in Edmonton and Calgary

	Edmonton central* Jan 3, 1995 to Dec 26, 2000	Edmonton east* Jun 6, 1993 to Dec 26, 2000	Calgary* Jan 3, 1995 to Dec 26, 2000
Minimum	0.29	0.12	1.18
Maximum	71.53	48.73	30.65
Average of available data	7.28	4.31	7.46
Per cent of readings less than 10 μg m^{-3}	85.5	90.9	83.1

*Values are monitoring data for a sample period of 24 hours once every 6 days for the period indicated. Data is reported in μg m^{-3}.

Data is from the Clean Air Strategic Alliance database.

The monitoring data for Edmonton and Calgary (Table 6.3) suggest that ethylene levels in the urban airmass are typically low. This may be due to ethylene-NO_x reactions. Note that these data do not provide an indication of the minimum or maximum ethylene levels that occurred during the day, since samples collected over an entire day were analyzed. Nevertheless, the data does indicate that the majority of the 24-hour samples collected resulted in readings less than 10 μg m^{-3}.

Colbeck and Harrison (1985) compared ambient air hydrocarbon concentrations in samples taken from urban and "polluted" rural (downwind of urban centres) locations. Rural air samples (considered to represent background levels) contained an average of 2 μg m^{-3} ethylene, while samples from urban locations averaged 49 μg m^{-3}. Polluted rural air samples contained 26 μg m^{-3}, indicating some dilution and degradation during transport from urban to rural locations. Average annual ethylene levels in the Sarnia, ON industrial area varied between 6 and 14 μg m^{-3} between 1978 and 1983 (Lambdon Industrial Society, 1983).

Ethylene levels in a suburban area of Philadelphia near several industrial facilities ranged from 6 to 117 μg m^{-3} (Giannovario *et al.*, 1976). The actual location, time of sampling (day, month, year) and sampling protocol were not described.

Ethylene concentrations of up to 805 μg m^{-3} have been detected in downtown Washington DC (Abeles and Heggestad, 1973). This is the highest ambient ethylene concentration reported in the literature. Levels diminished as the distance from the downtown core increased, reaching 45 μg m^{-3} outside the circumferential highway

Measurements of ethylene in the air near Swansea, South Wales indicated an average of 322 μg m^{-3} ethylene, with 230 μg m^{-3} in air samples taken on hillsides away from main roads and houses (Harbourne *et al.*, 1973). These are relatively high concentrations, and were attributed to heavy industrial and transportation activities.

In urban environments, peak ethylene levels generally correspond with peak traffic activity. In Hamburg, Germany, maximum concentrations of ethylene (173 μg m^{-3}) were observed near a city street during rush hour (Nassar and Goldbach, 1979). Peaks were observed during both the

morning (0900 to 1100 hr) and afternoon (1600 to 1900 hr) high-traffic periods. Levels at night fell to 12 to 23 μg m^{-3}, which for Hamburg, are close to local background concentrations. A similar pattern was observed near a service station, away from heavy traffic, although overall levels were lower, peaking at about 58 μg m^{-3}. Ethylene levels over a Pasadena CA highway increased within minutes of increased traffic flow, as measured using a bistatic laser system (Menzies and Shumate, 1976). Because only 20% of the laser path length was over the highway, the ethylene concentration at the edge of the road (9 to 39 μg m^{-3}) was underestimated in this study. Vegetation in the vicinity of larger roads may be expected to respond to regular ethylene exposures resulting from vehicular activity.

Near an industrial area of Hamburg, combined rural and residential emissions resulted in 23 μg m^{-3} ethylene, with an additional 23 μg m^{-3} coming from urban and industrial areas. It was hypothesized that some of the urban/industrial ethylene reacted photochemically prior to measurement; this was substantiated with the measurement of lower ethylene concentrations during the summer when solar radiation was at its highest (Nassar and Goldbach, 1979).

Ethylene levels of 18 μg m^{-3} were observed in Delft, The Netherlands (Bos *et al.*, 1977). Half of this amount was attributed to industrial sources, with the other half arising from automobiles.

6.3 Industrial Environments

Some industrial processes generate and emit ethylene into the air. The literature describing ambient ethylene levels in and around industrial areas is summarized in Table 6.4.

Table 6.4 Ethylene levels in ambient air in industrial environments

Location, Date, Time of Day	Ethylene (μg m^{-3})	Reference
Fort McMurray AB, 1980	16 (max)	Bottenheim (1984)
Industrial area near San Francisco CA, Sept. 1975	3.5 (max)	Sexton and Westberg (1979)
Trombay, Bombay, India, Dec. 1981	2 to 38	Mohan Rao *et al.* (1983)
Trombay, Bombay, India, Jan. 1982	5 to 137	
Trombay, Bombay, India, Monthly for 1100 to 1300 hr and 1430 to 1630 hr, 1982	2 to 44 (mean) 138 (max)	Netravalkar and Mohan Rao (1984)
NW England, Feb. to Mar. 1978		Harrison and Holman (1980)
Oil refinery	<6	
Fertilizer manufacturing facility	<1	
Near 1,1,1-trichloroethane, vinyl chloride monomer and perchloroethene manufacturing facility	<1 to 610	

Plume chemistry analyses of the emissions from the Syncrude and Suncor oil sands facilities in the Fort McMurray, Alberta area were conducted in the winter, spring and summer of 1980 (Bottenheim, 1984). Ethylene concentrations within the Syncrude plume ranged from 0.3 to

16 μg m^{-3}, with higher concentrations found nearer the source stack. The highest values tended to occur during the summer months.

Combined emissions from industrial facilities (petroleum refineries, power plants, chemical processing facilities and other industries) in the San Pablo Bay - Carquinez Strait - Suisun Bay channel (near San Francisco CA) increased ethylene levels. Observed concentrations were from below the limit of detection (0.5 μg m^{-3}) to up to 3.5 μg m^{-3} (Sexton and Westberg, 1979). Levels progressively increased as the number of sources contributing to the overall pollution burden increased.

Ethylene levels in Trombay, Bombay, India ranged from 2 to 38 μg m^{-3} in December 1981, and from 5 to 137 μg m^{-3} in January 1982 (Mohan Rao *et al.*, 1983). Trombay is located approximately 20 km from the city of Bombay, and is near two oil refinery sites. Most of the measurements indicated that only background levels of ethylene were present in the Trombay area. The source(s) that resulted in elevated ethylene levels was (were) not determined. Mean monthly ethylene concentrations for the periods of 1100 to 1300 hr and 1430 to 1630 hr ranged from 2 to 44 μg m^{-3} ethylene (Netravalkar and Mohan Rao, 1984). Individual daily measurements showed a maximum of 138 μg m^{-3}. The highest levels were recorded in February 1992, and the lowest in July 1992.

Ethylene levels downwind of a refinery (<6 μg m^{-3}), a fertilizer manufacturing facility (<1 μg m^{-3}), and in some small towns (pop. 4,500 to 8,600) and a small city (pop. 64,000) (<9 μg m^{-3}) were not above levels found in rural areas (14 μg m^{-3}) (Harrison and Holman, 1980). However, levels around a facility manufacturing 1,1,1-trichloroethane, vinyl chloride monomer, and perchloroethene varied between <1 μg m^{-3} to 610 μg m^{-3}, with the highest concentrations occurring at the point of impingement of the plume from the three facility stacks.

6.4 Other Environments

Gases produced from covered, vented landfills may contain ethylene. The amount of ethylene generated and released varies with the types of material in the landfill, the age of the landfill, and the design and methods used to build and seal the site. The gas in venting pipes in the Gin Drinkers Bay landfill, Hong Kong, included an average of 2,300 μg m^{-3} ethylene; however, the pipes varied greatly in ethylene content (Wong and Yu, 1989a). Ethylene also escaped through the surface of the covering soil, since a gas preventing blanket was not used to seal the landfill (Wong and Yu, 1989b). In neither of these studies (Wong and Yu, 1989a, b) was total ethylene emission from the landfill calculated.

Bausher (1991) measured soil gas concentrations over and near landfill sites in Florida. Levels as high as 85,100 μg m^{-3} ethylene were observed in gas sampling tubes in the immediate area of the landfills, with levels in the soil diminishing as the distance from the landfill increased. No ambient air ethylene concentrations were reported. Valencia orange trees in the area of the landfill showed signs characteristic of ethylene exposure (wilting, leaf abscission). Since other gases (oxygen, carbon dioxide, methane) also varied with the distance from the landfill, separating the effects and attributing some or all of them to ethylene is not possible.

7.0 ENVIRONMENTAL EFFECTS OF ETHYLENE

There have been many research projects devoted to determining the role of ethylene in plant growth and development; however, most studies presented in the literature contain data resulting from exposure of plants to concentrations well in excess of those expected to occur in ambient air. On the other hand, it must be noted that complete removal of ethylene from the atmosphere can also result in detrimental effects on plant growth (Reid and Watson, 1985). The following review emphasizes the results from studies in which lower levels of ethylene were used (equal to or less than 1,150 $\mu g\ m^{-3}$), although results of experiments in which higher levels were used are presented for comparison.

7.1 Microorganisms

No information regarding the effect(s) of ethylene at ambient levels less than 1,150 $\mu g\ m^{-3}$ was found. Some evidence of the fungistatic effects of ethylene was reviewed by the National Research Council of Canada (1985), with the conclusion that the evidence for ethylene fungistasis is weak. Ethylene does have an effect on the nodulation of legume roots by root nodulating bacteria, and may affect the interaction of plant roots with other soil microorganisms. These data are discussed in *Section 7.2.4, Plant Growth*.

7.2 Plants

As indicated previously, plants naturally produce ethylene that can act as a plant hormone. Ethylene in plant tissues can either influence or be influenced by other plant hormones. For example, increased ethylene concentrations can induce production of giberellic acid (Rijinders *et al.*, 1997). Alternatively, ethylene production can be induced by auxin (Grossmann and Hansen, 2001). Induced ethylene can regulate leaf abscission, epinastic growth, or play a role in developmental processes such as bud formation and growth, promotion or inhibition of flowering, feminization, and senescence (Grossmann and Hansen, 2001). The remainder of this section discusses the effects of ethylene on different aspects of plant growth and metabolism.

7.2.1 Germination

Increased seed germination in some species has been observed in response to ethylene, while in other species ethylene either retards germination or has no effect (Table 7.1). Injections of ethylene (1,150 $\mu g\ m^{-3}$ and above) into the soil in pots containing seeds of redroot pigweed (*Amaranthus retroflexus* L.) and large and small seeds of common cocklebur (*Xanthium pensylvanicum* Wallr.) increased total germination (Egley, 1980). Ethylene injections of 1,150 $\mu g\ m^{-3}$ and above promoted germination in several other species, while not affecting many others (Taylorson, 1979). These experiments were conducted to investigate the potential for stimulating weed germination, rather than to determine the lowest concentration of ethylene that would have an effect. Germination of redgrass (*Themeda triandra*), an African fire-climax grass, was not affected by ethylene in the concentration range of 1 to 1,150,000 $\mu g\ m^{-3}$ (in 10-fold

increments) or by application of ethephon in a similar range of concentrations (Baxter *et al.*, 1994). [See *Section 3.2.3, Other Sources* for a description of ethephon.] Lettuce seed germination was promoted by exposure to smoke; however, exposure to ethylene (5,750 to 115,000 μg m^{-3}) did not stimulate germination to the same degree (Jäger *et al.*, 1996). Thus, the ethylene component of smoke (from burning vegetation) does not appear to be responsible for the stimulation of germination in response to smoke exposure.

Table 7.1 Effects of ethylene on germination

Species	Ethylene (μg m^{-3})	Exposure Method	Effect	Reference
Redroot Pigweed (*Amaranthus retroflexus*) Cocklebur (*Xanthanum pensylvanicum*)	>1,150	Flasks (light and dark)	Increased 2 to 6 fold Increased 2 to 7 fold	Egley (1980)
Redroot Pigweed (*Amaranthus retroflexus*) Tumble Pigweed (*Amaranthus spinosus*) Ragweed (*Ambrosia artemisiifolia*) Lambsquarters (*Chenopodium album*)	>1,150	Sealed flasks (light and dark)	Promotive	Taylorson (1979)
Purslane (*Portulaca oleracea*)	>1,150	Sealed flasks (light)	Promotive	Taylorson (1979)
Red sorrel (*Rumex acetosella*) Curly dock (*Rumex crispus*) Broadleaf dock (*Rumex obtusifolius*)				
Rough cinquefoil (*Potentilla norvegica*)	>1,150	Sealed flasks (light and dark)	Inhibitory	Taylorson (1979)
Horsenettle (*Solanum carolinense*)				
10 grass species	>1,150	Sealed flasks (light and dark)	No effect	Taylorson (1979)
21 broadleaf species				
Redgrass (*Themeda triandra*)	1.15 to 1,150,000	Sealed flasks	No effect	Baxter *et al.* (1994)
Lettuce (*Latuca sativa* cv. Grand Rapids)	1,150 to 2,300 5,750 to 115,000	Sealed chambers	No effect Promotive	Jäger *et al.* (1996)

7.2.2 Photosynthesis

Ethylene may affect photosynthesis by one or more mechanisms. The effect may be on CO_2 uptake (Pallas and Kays, 1982; Squier *et al.*, 1985). Ethylene (112 to 589 μg m^{-3}) may affect carbon assimilation by inhibiting RuBP-carboxylase activity (the enzyme which fixes CO_2 within the plant cell) (Squier *et al.*, 1985). Ethylene may also reduce CO_2 fixation by inhibiting electron transport in the light reactions. Thus, reducing the conversion of light energy into chemical energy in the plant cell resulting in less chemical energy to devote to CO_2 fixation (Wullschleger *et al.*, 1992). Ethylene exposure may also alter distribution of fixed carbon in plants. Redistribution of photosynthate within plants has been observed following treatment with ethephon, a compound that releases ethylene after uptake and degradation (Woodrow *et al.*, 1988). Each of these effects has been demonstrated to occur in one or more species; however,

given the physiological complexity of photosynthesis and photosynthate partitioning, there has been insufficient research to determine if the observed effects are general across the plant kingdom, or represent species-specific responses to ethylene exposure.

The literature describing the effects of ethylene on photosynthesis is summarized in Table 7.2. As described in *Section 3.2, Anthropogenic Production of Ethylene*, vehicular exhaust is the major man-made source of ethylene. The highest levels of ethylene in urban centres occur in the morning and late afternoon, coincident with periods of active photosynthesis.

A 28-hour exposure of soybean (*Glycine max* L.) to ethylene reduced photosynthesis of plants in all treatments > 112 $\mu g\ m^{-3}$ relative to that of the control (Squier *et al.*, 1985). By the end of the fumigation period, photosynthesis in the control plants had increased by 20%, while photosynthesis in plants exposed to 112 and 281 $\mu g\ m^{-3}$ ethylene remained constant during this period. Thus, relative to the control, exposure to 112 and 281 $\mu g\ m^{-3}$ ethylene resulted in a statistically significant reduction in photosynthesis. However, plants exposed to 589 $\mu g\ m^{-3}$ ethylene exhibited a 50% reduction in photosynthesis relative to the initial rate, well below the rate in control plants at the end of the experiment.

Photosynthesis in peanut (*Arachis hypogaea* L.) rapidly decreased after the initiation of fumigation with 281 and 589 $\mu g\ m^{-3}$ (Squier *et al.*, 1985). Photosynthesis in peanut plants exposed to 112 $\mu g\ m^{-3}$ remained relatively constant, while an 8 to 12% increase was observed in control plants. By the end of the 28-hour treatment period, plants treated with 112 $\mu g\ m^{-3}$ had recovered to the control photosynthetic rate, while plants exposed to 281 and 589 $\mu g\ m^{-3}$ remained 40 to 50% below the initial rate. Inhibition (33% reduction) of photosynthesis in peanut was observed by Kays and Pallas (1980) following treatment of 3-week old peanut leaves with 288 $\mu g\ m^{-3}$ ethylene for 2 hours. A response was not observed at 115 $\mu g\ m^{-3}$, and was saturated at 1,150 $\mu g\ m^{-3}$. Photosynthetic inhibition was increased by longer ethylene exposures. Photosynthesis returned to normal in all plants treated for short periods of time (0.5 to 2 hours). A constant level of inhibition (18%) was observed at several light intensities; thus, the effect is not expected to differ under brighter or cloudier conditions. Inhibition of photosynthesis in peanut leaves occurred rapidly after exposure to 1,150 $\mu g\ m^{-3}$ ethylene (Pallas and Kays, 1982). Photosynthesis was reduced by as much as 68% after a 6-hour exposure. Photosynthesis in leaves exposed for less than 6 hours had fully recovered by the following day but plants in the 6-hour treatment required an additional day for recovery. Decreased photosynthesis in 8 cultivars of peanut by a 2.5-hour ethylene exposure (1,150 $\mu g\ m^{-3}$) was observed, and ranged from a 10 to 35% inhibition (Pallas and Kays, 1982). Leaf age was not a factor in this response. Stomatal conductance was reduced in peanut leaves treated with 1,150 $\mu g\ m^{-3}$ for 2.5 and 6 hours, with stomatal closure being greater on the lower surface of the leaf. Stomatal opening correlated with recovery in photosynthesis.

Tobacco (*Nicotiana tobaccum* L.) required higher concentrations of ethylene than peanut or soybean to induce similar photosynthetic effects (Squier *et al.*, 1985). Photosynthesis in tobacco plants treated with 589 $\mu g\ m^{-3}$ remained at near control levels through the first photoperiod (0800 to 1600 hr), but declined to about 40% of that in controls by the end of the 28-hour treatment. In

Table 7.2 Effects of ethylene on photosynthesis

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Exposure Method	Effect	Reference
Soybean (*Glycine max*)	112	28 hours	Continuously stirred tank reactor	20% decrease	Squier *et al.* (1985)
	281			20% decrease	
	589			50% decrease	
Peanut (*Arachis hypogaea*)	115	2 hours	Fumigation chamber	No effect	Kays and Pallas (1980)
	288			33% Decrease	
Peanut (*Arachis hypogaea*)	112	28 hours	Continuously stirred tank reactor	8 to 12% decrease	Squier *et al.* (1985)
	281 to 589			40 to 50% decrease	
Peanut (*Arachis hypogaea*)	1,150	2.5 hours	Attached leaf in assimilation chamber	10 to 35% decrease	Pallas and Kays (1982)
		6 hours		68% decrease	
Tobacco (*Nicotiana tobaccum*)	589	28 hours	Continuously stirred tank reactor	40% decrease	Squier *et al.* (1985)
	1,150			>80% decrease	
	2,300			>80% decrease	
Green ash (*Fraxus pensylvanica*)	281	28 hours	Continuously stirred tank reactor	10% decrease	Squier *et al.* (1985)
	589			10% decrease	
Corn (*Zea mays*)	≤4,600	28 hours	Continuously stirred tank reactor	No effect	Squier *et al.* (1985)
Potato (*Solanum tuberosum*)	575	3 hours	Attached leaf in sealed cuvette	10% Decrease	Govindarajan and Poovaiah (1982)
	1,150	3 hours		18% Decrease	
Potato (*Solanum tuberosum*)	1,150	2.5 hours	Attached leaf in assimilation chamber	No effect	Pallas and Kays (1982)
Jerusalem artichoke (*Helianthus tuberosus*)				7% Decrease	
Sunflower (*Helianthus annuus*)				12% Decrease	
Sweet potato (*Ipomoea batatas*)				10% Decrease	
Green bean (*Phaseolus vulgaris*)				No effect	
Pea (*Pisum sativum*)				No effect	
Sensitive plant (*Mimosa pudica*)				No effect	
White clover (*Trifolium repens*)				No effect	

plants exposed to 1,150 and 2,300 $\mu g\ m^{-3}$, photosynthesis declined immediately upon exposure to ethylene, and continued to decline to less than 20% of controls by the end of the experiment.

Green ash (*Fraxinus pennsylvanica* L.) was not as affected by ethylene as soybean, peanut and tobacco. Slight decreases in photosynthesis were observed immediately after initiation of

treatment with 281 and 589 μg m^{-3} ethylene, but ash seedlings retained approximately 90% of the control photosynthetic rate through the course of the experiment (Squier *et al.*, 1985).

Photosynthesis in corn (*Zea mays* L.) was not affected by concentrations up to 4,600 μg m^{-3} (Squier *et al.*, 1985).

Exposure of potato (*Solanum tuberosum* L.) leaves to 575 to 1,150 μg m^{-3} ethylene reduced net carbon assimilation by 10 to 18% (Govindarajan and Poovaiah, 1982). Concentrations in excess of 1,150 μg m^{-3} did not further affect the response. The initial effect was observed after a 1.5- to 2-hour lag period. As stomatal aperture was not affected by ethylene in this study, the ethylene likely interfered with CO_2 assimilation in a manner other than by stomatal control; however, activity of RuBP-carboxylase was not altered by the ethylene treatment.

Ethylene concentrations up to $1.15 \cdot 10^8$ μg m^{-3} did not affect airflow through the stomates of corn seedlings (Pallaghy and Raschke, 1972). While stomatal effects were apparent in the studies of Squier *et al.* (1985), direct effects of ethylene on carbon assimilation may also have occurred. High ethylene concentrations (11,500 μg m^{-3}) have been shown to inhibit photosynthetic electron transport in the light reactions in soybean; thereby, reducing available cellular energy for carbon assimilation (Wullschleger *et al.*, 1992).

Photosynthesis in Jerusalem artichoke (*Helianthus tuberosus* L.), sunflower (*Helianthus annuus* L.) and sweet potato (*Ipomoea batatas* L.) was also inhibited by a 2.5 hour exposure to 1,150 μg m^{-3} ethylene; however, the effect was less than that observed in peanut (Pallas and Kays, 1982). In addition, there was no effect of 1,150 μg m^{-3} ethylene (for 2.5 hours) on photosynthesis in green bean (*Phaseolus vulgaris* L.), scarlet runner bean (*P. coccineus* L.), pea, Irish potato (*Solanum tuberosum* L.), sensitive plant (*Mimosa pudica* L.) and white clover (*Trifolium repens* L.).

The study by Squier *et al.* (1985) is one of the few which have employed treatment concentrations that are comparable to those found in ambient air in urban and industrial areas. While the treatments used were short-term continuous exposures, which did not follow the patterns found in most urban areas (morning and afternoon peaks), the treatment concentrations did approximate those found during the light period when photosynthesis and carbon assimilation is active. These results strongly indicate that ethylene concentrations in the range of 112 to 2,300 μg m^{-3} will affect photosynthesis, and hence growth, of some plant species.

7.2.3 Respiration

Ethylene effects on dark respiration (CO_2 release from plants in the dark) and activity of the individual enzymes in the pentose phosphate pathway in 8-day-old pea seedlings exposed to 11.4, 114 and 1,135 μg m^{-3} ethylene for 48 hours were reported by Ageev *et al.* (1996) (Table 7.3). At 11.4 μg m^{-3}, CO_2 evolution from pea seedlings increased relative to CO_2 evolution from peas kept in an ethylene-free chamber. At 114 μg m^{-3}, CO_2 evolution remained the same as at 11.4 μg m^{-3} (significantly higher than in the ethylene-free treatment), while alcohol

dehydrogenase (ADH) enzyme activity increased by a factor of 4. Increased ADH activity is indicative of a shift in plant metabolism resulting from anaerobic conditions (reduced oxygen availability). Although the precise role is unknown, ethylene plays a role in responses of plants to anaerobic conditions.

Table 7.3 Effect of ethylene on respiration and alcohol dehydrogenase activity†

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Exposure Method	Respiration (% of Control)	ADH Activity (% of Control)
Pea (*Pisum sativum*)	11.4	48 hours	Fumigation	180	124
	114		chamber	190	407
	1,135			210	201

† Data from Ageev *et al.* (1996)

7.2.4 *Plant Growth*

Ethylene exposure may affect root growth, shoot growth, or other processes involving roots and shoots (e.g. interactions between roots and microorganisms) (Table 7.4).

Root elongation in 48-hour-old corn seedlings was inhibited at ethylene concentrations of 115 $\mu g\ m^{-3}$ and above (Whalen and Feldman, 1988). Ethylene was applied to germinating corn seed in a sealed test tube. Inhibition occurred within 20 minutes after initial exposure, and growth returned to normal within 15 minutes of removal of ethylene. The response saturated at 6,900 $\mu g\ m^{-3}$. Barley (*Hordeum vulgare* L.) seminal roots showed significantly reduced growth following a 21-day treatment with up to 11,500 $\mu g\ m^{-3}$ ethylene (Crossett and Campbell, 1975). Barley would only be affected if conditions were such that ethylene built up to these high levels in the soil. These circumstances would occur naturally only under extreme conditions (e.g. in flooded soils) rather than as a result of human activity. Ethylene at 115, 1,150 and 5,750 $\mu g\ m^{-3}$ in the gas stream bubbled though the nutrient medium for 7 to 14 days of hydroponically grown corn (4-leaf stage) inhibited seminal root elongation by 15 to 68% and dry weight accumulation by 12 to 19% (Jackson *et al.*, 1981). Ethylene at 115 $\mu g\ m^{-3}$ did not have a statistically significant effect on corn root growth but this concentration resulted in a significant reduction in leaf extension after 14 days exposure.

Tomato (*Lycopersicon esculentum* Mill.) root elongation was stimulated by 15% following a 24-hour exposure to 23 $\mu g\ m^{-3}$ ethylene (Konings and Jackson, 1979). In addition, root elongation was increased relative to control by 2, 3 and 4-day exposures to 23 $\mu g\ m^{-3}$ ethylene. Significant inhibition of root elongation occurred at concentrations of 58 $\mu g\ m^{-3}$ and above. Growth of ethylene-treated rice (*Oryza sativa* L.), roots increased following 24-hour exposures to 23, 58 and 173 $\mu g\ m^{-3}$ ethylene. Conversely, growth was inhibited at 1,150 $\mu g\ m^{-3}$ ethylene. Roots of white mustard (*Sinapis alba* L.) were not affected by exposure to 23 $\mu g\ m^{-3}$ for 24 hours; however, root elongation was significantly inhibited (by 20%) at 58 $\mu g\ m^{-3}$, by 50% at 173 $\mu g\ m^{-3}$, and by 77% at 1,150 $\mu g\ m^{-3}$.

Table 7.4 Ethylene effects on root and shoot growth

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Exposure Method	Effect	Reference
Corn (*Zea mays*) 4 leaf stage	115 1,150 5,750	7-14 days	Bubbled through hydroponic solution	15%, 51% and 68% reduction in root length Significant inhibition of leaf extension at 115 $\mu g\ m^{-3}$	Jackson *et al.* (1981)
Corn (*Zea mays*)	≥115	24 hours	Sealed test tubes	Significant reduction of root growth	Whalen and Feldman (1988)
Barley (*Hordeum vulgare*)	1,150 to 11,500	7 to 21 days	Bubbled through hydroponic solution	Inhibition of seminal root growth and reduced root and shoot dry weight	Crossett and Campbell (1975)
Tomato (*Lycopersicon esculentum*)	23	1-4 days	Fumigation of roots in sealed chamber	Significant increase of root elongation	Konings and Jackson (1979)
	58	1-4 days		Significant inhibition of root elongation	
White Mustard (*Sinapis alba*)	58 to 1,150	24 hours		Inhibition of root growth	
Rice (*Oryza sativa*)	23 to 173 1,150	24 hours 24 hours		Promotion of root growth Inhibition of root growth	
Rice (*Oryza sativa*) Barnyard grass (*Echinochloa oryzoides*)	1,135	3 days	Flow-through chamber	Promotion (61%) of coleoptile growth Inhibition of mesocotyl growth	Pearce *et al* (1992)
Rice (*Oryza sativa*)	1,150	1-6 days	Sealed containers	Increased coleoptile growth and polyamine content	Lee and Chu (1992)
Pea (*Pisum sativum*)	11,500	7 weeks	Roots fumigated in sealed chambers	Reduced root nodulation and 50% reduction in root growth after 12 d exposure	Goodlass and Smith (1979)
Clover (*Trifolium repens* L.)	11,500	6 weeks		Reduced root nodulation	
Pea (*Pisum sativum*)	81 253 518	3 weeks	Forced through rooting medium	50% reduction in root nodulation 94% reduction in nodulation 40% reduction in growth	Lee and LaRue (1992b)
Sweet clover (*Melilotus alba* U389)	81	3 weeks		Almost complete inhibition of root nodulation	
Soybean (*Glycine max*)	518	3 weeks		No effect on nodulation Root and shoot dry weight decreased and primary root length reduced	
Pea (*Pisum sativum*)	23 to 46	7 days	Fumigation of seedlings in the dark	Threshold for inhibition of growth and geotropism in epicotyl and root	Goeschl and Kays (1975)
Peanut (*Arachis hypogaea*)	46-368	7 days		Threshold for inhibition of root and shoot growth	
Bean (*Phaseolus vulgaris*)	92 to 184	7 days		Threshold for inhibition of root and shoot growth	
Cotton (*Gossypium hirsutum*)	184 to 368	7 days		Threshold for inhibition of root and shoot growth	
American beachgrass (*Ammophila breviligulata*)	1,150	6 weeks	Gas-tight Perspex cylinders	Increased formation of stem nodes , inhibited internode elongation and reduced lamina growth	Voesenek *et al.* (1998)

Interactions between plant roots and soil mycorrhizae are important to the health and growth of plants. Ethylene has been observed to affect this association at concentrations at or above 92,000 μg m^{-3} (Tosh *et al.*, 1994). The effects of ethylene at levels 100 to 1,000-fold lower (as would be found in ambient air) were not determined. Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) seedlings were treated with ethephon to generate ambient soil concentrations of ethylene of 7 to 575 μg m^{-3} (Graham and Linderman, 1981). Root growth of the seedlings was promoted at concentrations of 12 to 58 μg m^{-3} ethylene, was not affected between 58 and 173 μg m^{-3}, and was inhibited above 173 μg m^{-3}. In addition, mycorrhizal infection of the roots was not affected by ethylene (ethephon) treatment, but root infections by pathogenic fungi were increased at 115 μg m^{-3} ethylene. Ethylene treatments were not continuous, as ethephon degrades rapidly within plant tissues the first few days after application (Graham and Linderman, 1981; Foster *et al.*, 1992). In some cases, a second application of ethephon to the soil was required to maintain the ethylene concentration applied to the roots. It is unclear whether ethylene release from ethephon occurred in the soil, or was a function of degradation within the root cells. This complicates interpretation of this data, and this study is not included among those summarized in Table 7.3.

Nodulation of pea roots is inhibited by ethylene (Goodlass and Smith, 1979; Lee and LaRue, 1992b). Treatment of roots for seven weeks with 11,500 μg m^{-3} ethylene, beginning when the plants were 4 weeks old, reduced nodulation by 75% (Goodlass and Smith, 1979). Root growth was affected only slightly, but shoot growth was reduced by 30 to 50%. Continuous exposure of the root zone of the pea cultivar Sparkle to ethylene for 21 days (from planting to harvest), reduced the number of nodules per plant (Lee and LaRue, 1992b). The number of nodules was reduced from 306 (control plants) to 145 at 80 μg m^{-3} ethylene. There was practically no nodulation observed at 516 μg m^{-3} ethylene; in contrast, root growth was reduced by 51% in length and 31% in dry weight while shoot dry weight was reduced by 50% at this concentration of ethylene (Lee and LaRue, 1992a). Similar results were obtained using the other pea genotypes Rondo, Sparkle E135F (a mutant which forms small ineffective nodules), the hypernodulating genotype Rondo nod-3 (Lee and LaRue, 1992b), and the low nodulation mutant R82 (Lee and LaRue, 1992a).

Thus, nodulation responses are general, and not restricted to one pea genotype. Nodulation of sweet clover was found to be more sensitive than pea (Lee and LaRue, 1992b), with nearly complete inhibition of nodulation occurring at and above 80 μg m^{-3} ethylene, while primary root growth, root dry weight and shoot dry weight were reduced to the same extent as the pea cultivar Sparkle. Root growth in soybean was reduced to the same extent as sweet clover and pea by concentrations of ethylene up to 516 μg m^{-3}, while nodulation was not reduced in this species (Lee and LaRue, 1992b). Treatment of soybean roots with ethephon at levels which significantly reduced shoot growth and plant wet and dry weights did not reduce nodulation (Hunter, 1993). At very high levels of ethephon (1,000 μM), root growth, lateral root number and nodulation were reduced; however, in this study the effect of ethephon (ethylene) on nodulation was likely non-specific (i.e. reduced nodulation was an indirect effect).

Mutants of *Rhizobium leguminosarum* bv. *viciae* which are reduced in their ability to effectively induce nodulation in vetch (*Vicia sativa* spp. *nigra*) were even less able to induce nodulation in the presence of ethylene (van Workum *et al.*, 1995). Ethylene removal by addition of AVG (1-aminoethoxyvinyl glycine; an ethylene biosynthesis inhibitor) increased effective nodulation in vetch (van Workum *et al.*, 1995) and in *sym-5* mutants of Sparkle pea (Fearn and LaRue, 1991). However, while AVG treatment of soybean reduced ethylene production, it did not affect inoculation by *Bradyrhizobium japonicum* (Suganuma *et al.*, 1995). As with many other plant responses involving ethylene, the role of ethylene in nodulation appears to vary by species (both plant and microorganism).

Mesocotyl, but not coleoptile, growth in seedlings of barnyard grass (*Echinochloa oryzoides* [Ard.] Fritsch) was inhibited 24% by treatment with 1,135 $\mu g\ m^{-3}$ ethylene for 3 days (Pearce *et al.*, 1992). When applied to seedlings of rice, this concentration increased coleoptile extension by 61% (Pearce *et al.*, 1992). Stimulation of coleoptile growth in rice in response to 1,150 $\mu g\ m^{-3}$ ethylene was observed by Lee and Chu (1992), and this increase was coincident with increases in polyamine (spermidine and putrescine) content.

Voesenek *et al.* (1998) found that exposure of *Ammophila breviligulata* (American beachgrass) to 1,150 $\mu g\ m^{-3}$ ethylene for six weeks caused significant increases in stem node formation. In addition, they observed inhibition of internode elongation and significant decreases in lamina growth, especially of the youngest leaves.

Leaf growth in corn (4-leaf stage) was inhibited by bubbling 115 $\mu g\ m^{-3}$ ethylene through the nutrient medium for 14 days (Jackson *et al.*, 1981). Higher concentrations (1,150 and 5,750 $\mu g\ m^{-3}$) further reduced growth. Root fumigations at these levels would be very rare under field conditions.

In an attempt to understand ethylene effects on physiological mechanisms, Goeschl and Kays (1975) investigated the growth of roots and stems in pea, peanut, bean, and cotton (*Gossypium hirsutum* L.) seedlings in response to a range of ethylene concentrations. Pea epicotyl geotropism, epicotyl elongation, root elongation, epicotyl diameter, root geotropism and root diameter exhibited half-maximal responses at 109, 124, 351, 368, 380, 426 $\mu g\ m^{-3}$, respectively. The thresholds for these responses were in the range of 23 to 46 $\mu g\ m^{-3}$. The half-maximal concentrations inhibiting bean hypocotyl elongation, hypocotyl diameter, and root elongation were 380, 449, and 529 $\mu g\ m^{-3}$; the thresholds for these responses were between 92 and 184 $\mu g\ m^{-3}$. The threshold levels for hypocotyl elongation, hypocotyl diameter, and root elongation in peanut seedlings were between 46 and 368 $\mu g\ m^{-3}$. Higher levels of ethylene were required to elicit half-maximal responses in cotton: 644 $\mu g\ m^{-3}$ for cotton hypocotyl elongation, 702 $\mu g\ m^{-3}$ for root elongation, and 1,553 $\mu g\ m^{-3}$ for hypocotyl diameter, with thresholds between 184 and 368 $\mu g\ m^{-3}$. Some responses (e.g. geotropism in hypocotyls of bean, cotton and peanut) were not observed at concentrations of up to 11,776 $\mu g\ m^{-3}$. Although conditions used were very artificial relative to those found in the field (treatment of very young etiolated seedlings), these results indicate that some plants respond to very low levels of ethylene.

Abeles and Heggestad (1973) investigated the effects of ethylene on growth, development and reproduction in a number of species. Bean, African violet (*Viola* sp.), cucumber (*Curcurbita pepo*), marigold (*Tagetes erecta* L.), soybean, spring wheat (*Triticum aestivum* L.), petunia (*Petunia nyctaginiflora* Juss), honey locust (*Gleditsia triancanthos* L.), and tomato were grown in sealed fumigation chambers and exposed to concentrations of ethylene observed in the ambient air in Washington DC. While there was some variability in the responses among species, the general conclusion was that the threshold level for an ethylene effect was 12 $\mu g\ m^{-3}$, with a half-maximal response between 115 and 575 $\mu g\ m^{-3}$, and saturation above 1,150 $\mu g\ m^{-3}$. As a result, levels observed in the air in Washington DC were expected to have an effect on area vegetation. However, as this study was not properly replicated and statistically analyzed, these data can only be used as background information.

Ethylene levels rose to an estimated 115 to 230 $\mu g\ m^{-3}$ in a sealed growth chambers used for growing wheat (Martin and Sinnaeve, 1987); presumably these levels originated from the wheat plants. Growth was described as very poor and improved dramatically following the installation of an ethylene removal system containing acid permanganate on activated alumina. Re-circulation of the chamber air through the ethylene trap lowered ethylene levels to below the limit of detection of 12 $\mu g\ m^{-3}$. Growth of the wheat improved markedly within 48 hours of installing the purification system. Wheeler *et al.* (1996) also observed increased ethylene concentrations in a closed hyperbaric chamber used for growing wheat. Ethylene levels reached a maximum of 138 $\mu g\ m^{-3}$. It was concluded that the wheat was producing the ethylene. In addition, leaves exhibited longitudinal, epinastic rolling that was attributed to the increased ethylene concentration. In subsequent experiments installation of permaganate filters maintained ethylene levels below 46 $\mu g\ m^{-3}$.

Ethylene emission from landfills may also negatively affect plant growth. Ethylene escaping from vent pipes, and through the covering soil, was proposed as a contributing factor to poor plant growth on the covered Gin Drinkers' Bay landfill, Hong Kong (Wong and Yu, 1989b). Carbon dioxide, oxygen, methane and soil extractable lead also negatively affected plant growth. The amounts of ethylene in the ambient air, and in the soil, were not given.

7.2.5 Abscission and Senescence

The longevity of cut flowers may be affected by ethylene (Table 7.5); as a result, ethylene effects on flowers are an important economic consideration in the horticulture industry. The effects of ethylene on senescence and abscission are complex, and not fully understood. Flower sensitivity (abscission and senescence of the flower) varies by plant family, with some families being very sensitive (e.g. orchid, geranium, mint, and mallow families) relative to others (e.g. composite, parsley, and lily families) (Woltering and Van Doorn, 1988). Additionally, there may be large differences with respect to sensitivity to ethylene and senescence and abscission among plant species within a family, and between cultivars within a single species. A ranking of flower sensitivity in 93 species representing 22 plant families is presented in Woltering and Van Doorn (1988). As ethylene levels used to assess flower sensitivity were relatively high (3,405 $\mu g\ m^{-3}$) over a short treatment period (22 to 24 hours), these data are not representative of what one

Table 7.5 Effects of ethylene on abscission and senescence

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Exposure Method	Effect	Reference
Carnation (*Dianthus caryophyllus*)	58	48 hours	Dark fumigation of cut flowers	Increased flower senescence	Woltering and Harkema (1987)
	115	48 hours		Increased flower senescence	
	575	12 hours		Increased flower senescence	
Carnation (*Dianthus caryophyllus*)	≥115	24 hours	Dark fumigation of cut flowers	Increased flower senescence (cv. White Sim)	Woltering *et al.* (1993)
	≥265	24 hours		Increased flower senescence (cv. Chinera)	
	≥345	24 hours		Increased flower senescence (cv. Epomeo)	
Carnation (*Dianthus caryophyllus*)	35 to 69	48 hours		Increased flower senescence	US EPA (1978)†
	575	12 hours		Increased flower senescence	
Orchid	46 to 115	8 hours		Increased flower senescence	
	2 to 23	24 hours		Increased flower senescence	
Morning glory (*Ipomoea tricolor*)	12	≥1 hour	Dark fumigation of excised rib segments	Threshold for increased petal senescence	Hanson and Kende (1975)
	115	≥1 hour		Half-maximal exposure for petal senescence	
	11,500	≥1 hour		Saturation for petal senescence	
Morning glory (*Ipomoea tricolor*)	≥1,150	20 to 40 minutes		Increased flower fading	Kende and Baumgartner (1974)
Rose (*Rosa* spp.)	23	2 days	Fumigation of cut flowers	Inhibition of flower opening (cv. Lovely Girl)	Reid *et al.* (1989)
	≤1,1	2 days		Inhibition of flower opening (cv. Gold Rush)	
Begonia	173	10 days	Fumigation of whole plant	Increased flower abscission and reduced flower quality	Nowak and Fjeld (1993)
Easter lily (*Lilium longiflorum*)	58	77 days	Fumigation of whole plant	Flower stunting and distortion	Blankenship *et al.* (1993)
Pecan (*Carya illinoensis*)	115	14 days	Fumigation of intact shoots in the field	Increased shuck dehiscence (cv. Desirable)	Kays *et al.* (1975)
	288	14 days		Increased shuck dehiscence (cv. Big Z)	
Ficus (2 species)	575	48 hours	Fumigation chamber	5% Defoliation	Turner *et al.* (1988)
	19,550	48 hours		20% to 60% Defoliation	
English ivy (*Hedera helix* L.)	11,500			Increased leaf senescence	Horton and Bourguoin (1992)

† US EPA (1978) = US Environmental Protection Agency (1978)

would expect to see at ambient levels. Other research more relevant to environmental exposures is available, and is presented below.

Senescence of carnation (*Dianthus caryophyllus*) flowers in response to ethylene treatment was investigated by Woltering *et al.* (1993). Three cultivars of cut carnations were exposed to 12 to

12,650 μg m^{-3} ethylene in sealed chambers for 24 hours. Increased senescence of White Sim was observed above 115 μg m^{-3} ethylene, Chinera became senescent at 265 μg m^{-3}, and Epomeo at 345 μg m^{-3} ethylene. Irreversible wilting (senescence) of cut carnation flowers increased after a 48-hour exposure to 58 μg m^{-3} ethylene, a 24-hour exposure to 115 μg m^{-3} ethylene, and a 12-hour exposure to 575 μg m^{-3} (Woltering and Harkema, 1987). Confirmation of a proposed mathematical relationship between irreversible wilting, exposure time and ethylene concentration was not possible (Woltering and Harkema, 1987). Levels of up to 207 μg m^{-3} ethylene in the Denver metropolitan area did not affect carnation marketability since ethylene did not appear to affect the flowers while kept in cold storage (Hanan, 1973). However, longevity of flowers kept at room temperature is expected to decline during a period of severe pollution (Hanan, 1973).

Short (20- to 40-minute) exposures of excised morning glory (*Ipomoea tricolor*) flowers to concentrations of 1,150 μg m^{-3} ethylene and above hastened flower fading relative to controls (Kende and Baumgartner, 1974). Flower opening in rose cultivars (*Rosa* sp.) may be accelerated, inhibited, or unaffected in response to an exposure of 575 μg m^{-3} ethylene (Reid *et al.*, 1989). Flower distortion and abscission also occurred in some cultivars. Cultivars that were affected by ethylene were sensitive to low concentrations of the gas. Flower opening in Lovely Girl, one of the most sensitive genotypes, was inhibited by 23 μg m^{-3} ethylene, with maximum inhibition observed at 138 μg m^{-3} ethylene. The cultivar Gold Rush was not affected by ethylene at concentrations up to and including 1,150 μg m^{-3} (Reid *et al.*, 1989).

Rolling of petal rib segments excised from morning glory flowers has been used as a model to study flower senescence (Hanson and Kende, 1975). Treatment of rib segments with 12 μg m^{-3} increased the extent of rolling a small amount relative to the controls (exposed to air only). The onset of rolling occurred 1 hour earlier than the onset of rolling in the controls. Increasing ethylene concentrations up to 11,500 μg m^{-3} increased the extent of rolling (half-maximal response at 115 μg m^{-3}); although, the timing of the initiation of rolling was not altered by ethylene concentration. Early induction and increased rolling in response to ethylene closely paralleled the behaviour of the rib tissue during fading of the intact flower. Continuous treatment was not required. Rib tissues exposed for 1 to 1.5 hours exhibited early onset of rolling, and the extent of rolling was increased relative to controls; although, the maximum rolling response in short-term treatments was less than that observed in continuous treatments. Thus, short exposures to elevated ethylene levels may be sufficient to alter flower longevity in morning glory.

The keeping quality of potted flowers is also of considerable economic importance. Flower number and quality were reduced in two varieties of Begonia (*Begonia* x *cheimantha* and *B.* x *hiemalis*) following a 10-day exposure to 173 μg m^{-3} ethylene; although, one genotype (*B.* x *hiemalis*) was more sensitive than the other (Nowak and Fjeld, 1993). Flower abscission was the primary cause of lower flower numbers, since flower bud development was relatively unaffected. Partitioning of ^{14}C (supplied to the plant as $^{14}CO_2$) into the flower and flower buds was reduced by ethylene treatment; however, it is not clear if this was the primary mode of action of ethylene, or was a secondary effect following the onset of senescence and abscission. Long-term (77-day) exposure to 58 μg m^{-3} rendered Easter lily (*Lilium longiflorum* Thunb.) unmarketable due to severe stunting of growth and distortion of the flower (Blankenship *et al.*, 1993). Easter lilies

tolerated chronic ethylene levels of up to 12 μg m^{-3}. The treatment concentrations used in these experiments (Blankenship *et al.*, 1993; Nowak and Fjeld, 1993) are comparable to those found in urban areas. These experiments strongly suggest that the health of potted plants may be adversely affected by ethylene in urban settings.

Flowering (inhibition of flowering, or reduction in flower size) in petunia has been suggested as a possible means of monitoring ethylene levels in the environment (Posthumus, 1980). However, the response was poorly characterized, and a quantitative relationship between ethylene exposure and plant response was not presented.

Drying and bleaching of orchid sepals was reported to occur following an 8-hour exposure to 46 to 115 μg m^{-3}, or after a 24-hour exposure to 2 to 23 μg m^{-3} (Environmental Protection Agency, 1978). These results were not substantiated with a presentation of the data, but rather appeared as part of a review article (the original reference was not included).

Leaf senescence also increases in response to ethylene exposure. Leaf blade senescence in English ivy (*Hedera helix* L.) increased following a treatment with 11,500 μg m^{-3} (Horton and Bourguoin, 1992). This concentration is very high relative to ambient air ethylene levels.

Shuck dehiscence in pecan (*Carya illinoensis* [Wang.] K. Koch) increased following a 14-day exposure to 115 μg m^{-3} in one variety, and at 288 μg m^{-3} in a second variety (Kays *et al.*, 1975). In addition, leaf and fruit abscission increased following a 14-day treatment of 863 μg m^{-3} ethylene. While pecans do not grow in Alberta, these results show that different organs respond at different concentrations of ethylene, and that abscission of leaves and fruits may occur in response to levels of ethylene occasionally found in urban environments. Defoliation of two species of *Ficus* began at 575 μg m^{-3}, with 20% (*F. stricta*) to 60% (*F. benjamina*) defoliation occurring at 19,550 μg m^{-3} (Turner *et al.*, 1988). These levels are not expected to occur under ambient conditions.

7.2.6 Effects on Fruit and Yield

Initiation of ripening following ethylene exposure is one of the classic effects of this gas (Abeles *et al.*, 1992). Flores *et al.* (2001) used ethylene suppressed transgenic melons (*Cucumis melo* var. *cantalupensis* Nand) to determine the effects of externally applied ethylene on the ripening process. Fruit were exposed for five days to 115 to 57,345 μg m^{-3} ethylene. It was found that some of the ripening pathways (flesh softening, membrane deterioration) had an ethylene independent component (50 % inhibition in the absence of ethylene), while rind de-greening (yellowing) and peduncle detachment are dependent on ethylene. A linear increase in yellowing was observed within the range of 115 to 5,735 μg m^{-3} ethylene over the five-day exposure period. The ripening processes observed in this study were saturated at 2,867 or 5,735 μg m^{-3} ethylene.

As with senescence and abscission, there is limited data available for assessing the effects of ethylene on crop yield under ambient conditions. Ethylene effects are likely complex, depending upon environmental conditions, and vary by species and cultivar.

Removal of ethylene from air reduced the yield of canola and oat, relative to the yields of these crops grown under background ethylene levels (Table 7.6) (Reid and Watson, 1985). Ethylene-free air is a highly unnatural condition, and may have negatively affected plant growth and development. Thus, the treatment concentrations of 8 and 12 $\mu g\ m^{-3}$ are considered to be the controls, and effects of other ethylene treatments are compared to these levels.

Table 7.6 Effects of ethylene on oat and canola yield†

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Effect
Oat (*Avena sativa* L. cv. Random)	0	100 days	Per plant floret number increased by 29%
	8††	100 days	—
	40	100 days	Per plant floret number decreased by 26%
	81	100 days	Per plant floret number decreased by 89%
	173	100 days	Per plant floret number decreased by 99%
Canola (*Brassica campestris* L. cv. Candle)	0	87 days	Per plant seed yield reduced by 65%
	12††	87 days	—
	40	87 days	Per plant seed yield reduced by 52%
	173	87 days	Per plant seed yield reduced by 84%
	690	87 days	Per plant seed yield reduced by 99%

† Data from Reid and Watson (1985)

†† These levels are considered to represent local background ethylene concentrations; therefore, these levels are considered the control for the determination of effects of higher, and lower, ethylene concentrations.

Canola seed yield was reduced 84% or more, at exposures of 173 $\mu g\ m^{-3}$ (for 87 days) ethylene and above, while oat yield dropped substantially at 81 $\mu g\ m^{-3}$ (for 100 days) and above (Reid and Watson, 1985). While not as severe, seed yield in either crops dropped as ethylene levels rose from 8 to 40 $\mu g\ m^{-3}$ (oat) or 12 to 40 $\mu g\ m^{-3}$ (canola). Thus, 40 $\mu g\ m^{-3}$ is considered to be the level at which a negative effect occurred for both species.

7.2.7 Alberta Ethylene Crop Research Project

For the past several years, the focus of research efforts into the effects of ethylene has been to answer the question: Does ethylene affect plant growth and development? As a result, ethylene treatments given over short time periods have been high relative to the ambient air concentrations that plants are generally exposed to over longer periods of time. This has led to the understanding that ethylene is involved in a wide range of physiological processes, leading to effects visible at the morphological and anatomical levels.

To further the understanding of the effect of ethylene on crop plants, a research project (Alberta Ethylene Crop Research Project - AECRP) jointly sponsored by the provincial government and the petrochemical industries in Alberta, was directed towards answering the following questions.

- Are plants more susceptible to ethylene exposure at particular times during growth and development?
- What are the dose-response relationships between ethylene exposure and effects for a variety of species (crops, trees, native vegetation)?

Many types of facilities have been utilized for the study of air pollutants. Diesburg *et al.* (1989) specifically designed growth chambers for fumigation studies; in addition, Greenwood *et al.*, 1982; Heck *et al.*, 1988; Hendrey, 1993; Hendrey *et al.*, 1992; Runeckles *et al.*, 1990 designed exposure systems for field use (open-top chambers, ring fumigation systems). In order to meet the needs of the AECRP a gas exposure system was developed that could be used to expose plants to ethylene at accurate concentrations for specific durations (Archambault and Li, 1999a).

The study focussed on species and stages of growth that are most sensitive to ethylene. In order to determine what crops are sensitive to ethylene, and what the most sensitive growth stage is, eight cultivars of five species were tested for sensitivity (Archambault and Li, 1999b). Plants were treated with ethephon at one of seven different growth stages (Table 7.7). From the results of this study, it was recommended that barley cv. Harrington (spike emerging stage), canola cv. Quantum (many flowers open stage), and field pea (flat pods stage) be used for the ethylene exposure studies.

A brief summary of the experiments conducted to determine the dose response relationship of the tested species to ethylene is given in Table 7.8 (Archambault and Li, 2001). No significant effects were found for any of the measured parameters (Table 7.8), for ethylene concentrations up to 1,376 $\mu g\ m^{-3}$ for exposures up to 12 hours. However, significant yield reductions were observed at 57 $\mu g\ m^{-3}$ for barley, 57 $\mu g\ m^{-3}$ for canola, and 115 $\mu g\ m^{-3}$ for field pea with ethylene exposures of 3, 31 and 16 days, respectively.

The dose response experiments were designed based on the assumption that time of day does not affect plant sensitivity to ethylene. However, Tonneijck *et al.* (1999, 2000) observed greater epinastic response of potatoes to ethylene at night. As a result, the AECRP tested barley for response to 229 $\mu g\ m^{-3}$ ethylene for 30 days for one of 4 – 6 hour intervals (Table 7.8). It was found that barley was most sensitive to ethylene between 10:00 a.m. and 4:00 p.m. with up to 50% reductions in yield. Further experiments indicated that 5 consecutive exposures at 287 $\mu g\ m^{-3}$ ethylene from 10:00 a.m. to 4:00 p.m. also resulted in yield losses.

Table 7.7 Effect of time (growth stage) of ethephon exposure on reproduction

Growth Stage tested	Species	Stage effect observed
Cereals:		
Early leaf two stage	Barley (*Hordeum vulgare*)	
Main axix and two tillers stage	cv. AC Lacombe	No significant reductions
Flag leaf just visible stage	cv. Harrington	Spike emerging
Boots just visibly swollen		
First spike of inflorescence just visible	Wheat (*Triticum aestivum* L.)	
Beginning of anthesis	cv. CDC Teal	No significant reductions
Early milk	cv. AC Taber	No significant reductions
	Oats (*Avena sativa*)	
	cv. Derby	Flag leaf
Oilseeds:		
Second true leaf formed	Canola (*Brassica sp.*)	
Inflorescence visible at center of rosette	cv. Quantum (*B. napus*)	2nd true leaf or many flowers open
Lower buds yellowing		
First flower opening on terminal bud		
Many flowers opened		
Flowering complete		
Seeds in lower pods full size		
Legumes:		
First true leaf expanded (1 node)	Field pea (*Pisum sativum*)	
Fifth true leaf expanded (5 nodes)	cv. Carrera	No significant reductions
First buds visible		
First flower open		
Pods flat		
10 - 50% of pods on main stem full		
90 - 100% of pods on main stem full (pods yellowing)		

Table 7.8 Summary of ethylene exposures and effects on species tested in the Alberta Ethylene Crop Research Project

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Effect
Short term exposure			
Barley (*Hordeum vulgare* cv. Harrington) Field pea (*Pisum sativum* cv. Carrera) Canola (*Brassica napus* cv. Quantum)	†11.5 to 1,376	1.5 to 12 hr	No significant effect on measured parameters
White spruce (*Picea glauca*) Lodgepole pine (*Pinus contorta*)	11.5 to 1,376	1.5 to 12 hr	No significant effect on germination, vigour, or marketability
Long term exposure			
Barley (*Hordeum vulgare* cv. Harrington)	11.5 to 459	26 days	59% reduction in seed yield at 57 $\mu g\ m^{-3}$ nearly nil at 287 $\mu g\ m^{-3}$ and above
Barley (*Hordeum vulgare* cv. Harrington)	11.5 to 287	14 days	63% reduction in seed yield at 34.4 $\mu g\ m^{-3}$ 72% reduction in seed yield at 57 $\mu g\ m^{-3}$
Field pea (*Pisum sativum* cv. Carrera)	11.5 to 459	16 days	significant reduction in seed yield at 115 $\mu g\ m^{-3}$ when plants harvested at same time as controls
Canola (*Brassica napus* cv. Quantum)	11.5 to 459	31 days	Seed yield reduced up to 20% at 57 $\mu g\ m^{-3}$
Various long term exposures			
Barley (*Hordeum vulgare* cv. Harrington)	57	0 to 24 days	41% reduction in seed yield - 3 day exposure 89% reduction in seed yield - 24 day exposure
Field pea (*Pisum sativum* cv. Carrera)	57	0 to 28 days	No significant effects
Time of day exposures			
Barley (*Hordeum vulgare* cv. Harrington)	11.5 or 229	30 days for 1 of 4 - 6 hr periods: 4 am to 10 am 10 am to 4 pm 4 pm to 10 pm 10 pm to 4 am	50% reduction in seed yield for the 10 am to 4 pm exposure period
Different intervals between exposures			
Barley (*Hordeum vulgare* cv. Harrington)	229 or 574	5 - 6 hr exposures from 10 am to 4 pm with intervals of 0 to 11 days	Seed yield significantly reduced - intervals as long as 5 days did not allow complete recovery

† 11.5 $\mu g\ m^{-3}$ ethylene –This level is considered to represent local background ethylene concentrations; therefore, this level was used as the control ethylene concentration.

8.0 EFFECTS OF ETHYLENE ON HUMAN HEALTH

Ethylene is produced naturally in humans may be formed as a result of lipid peroxidation of unsaturated fats, oxidation of free methionine, oxidation of hemin in haemoglobin and metabolism of intestinal bacteria (Health Canada, 2001).

Ethylene has a long history of use as a clinical anaesthetic at high concentrations (80-90% in oxygen) with little associated toxicity (NRC, 1985; US EPA, 1992; Health Canada, 2001). The most probable route of human exposure to external ethylene is by inhalation. Of the ethylene inhaled only 2-3% is retained (Health Canada, 2001). Ethylene has low blood gas solubility; as a result, it is excreted rapidly and there is no evidence that it accumulates in the body. However, studies suggest that 2-3% of absorbed ethylene is metabolized to ethylene oxide. Of ethylene's primary metabolites, ethylene oxide is one that is of toxological concern as it has been shown to be genotoxic and carcinogenic in mice and rats (Health Canada, 2001). Pharmacokinetic studies of ethylene in rats indicate that exposure to 1,000 and 40 ppm (1,150,000 and 46,000 $\mu g\ m^{-3}$) ethylene are equivalent to exposure to 5.6 and 1 ppm ethylene oxide, respectively (Bolt and Filser, 1987). The authors concluded that these concentrations would not lead to a significant increase in tumors in ethylene exposed rats. In addition, the Office of Prevention, Pesticides and Toxic Substances (US EPA, 1992) indicated in their review of ethylene for use as a pesticide that the maximum exposure rate to ethylene under current use was 1,000 ppm (1,150,000 $\mu g\ m^{-3}$) (post-harvest treatment of stored commodities) and that no long-term problems had been attributed to the gas. It was indicated that their review relied primarily on published literature.

The research conducted on the effects of ethylene on humans and animals have in general used high ethylene concentrations (often in the 10^0's to 1,000's ppm) with little evidence of toxicity (NRC, 1985; US EPA, 1992; Health Canada, 2001). As the concentrations of ethylene that may affect human health are many fold higher than those that affect vegetation, the focus of this review was on vegetation effects.

9.0 GUIDELINES IN OTHER JURISDICTIONS

At present, an interim ethylene guideline that is protective of vegetation is in effect in Alberta, as outlined in Table 9.1.

Table 9.1 Alberta Ambient Air Ethylene Guideline (Interim)

Interim Ethylene Guideline	Averaging Period	Daytime Application Period	Seasonal Application Period
120 µg m^{-3}	6 hours	0300 to 2200 hours	May 1 through September 30, inclusive
50 µg m^{-3}	30 days	0300 to 2200 hours	May 1 through September 30, inclusive

Few other jurisdictions have a guideline for ethylene that is protective of vegetation. For comparison to the Alberta interim guideline, Table 9.2 summarizes the ethylene guidelines for those jurisdictions that do have guidelines in effect that are protective of vegetation.

Table 9.2 Summary of air quality guidelines for ethylene in other jurisdictions

Jurisdiction	Guideline (µg m^{-3})	Comments
Newfoundland	40	24 hour
Ontario	40	24 hour
The Netherlands	300	1 hour
	9	24 hours

It is recognized that an ambient objective may not be protective of every sensitive species, under all possible exposures; however, the ambient objective should be based on effects on species that are relevant to the jurisdiction. Tables 9.3 and 9.4 summarize the findings of studies that have been described in earlier sections of this report on the effects of ethylene on vegetation that can be grown in Alberta.

Table 9.3 Summary of ethylene effects on vegetation for ethylene exposures up to and including 48 hours

Reference	Species Description	Ethylene ($\mu g\ m^{-3}$)	Duration and Method of Exposure	Effect
Pallas and Kays (1982)	Sunflower (*Helianthus annuus* L. line CM90RR)	1,150	2.5 hours -Fumigation of attached leaves	12% reduction of photosynthesis
	Bean (*Phaseolus vulgaris* L. cv. Contender), Pea (*Pisum sativum* L. cv. Wando), White clover (*Trifolium repens* L.)	1,150	2.5 hours -Fumigation of attached leaves	No effect on photosynthesis
Hanson and Kende (1975)	Morning Glory (*Ipomoea tricolor* Cav.)	12	7 hours - Dark fumigation of excised rib segments	Rib rolling (senescence) increased relative to control
Archambault and Li (2001)	Barley (*Hordeum vulgare* cv. Harrington), Field pea (*Pisum sativum* cv. Carrera), Canola (*Brassica napus* cv. Quantum)	11.5 to 1,.376	12 hours - Fumigation	No effect on seed and head numbe or weight
	White spruce (*Picea glauca*), Lodgepole pine (*Pinus contorta*)	11.5 to 1,376	12 hours - Fumigation	No effect on germination, vigour a growth
Woltering *et al.* (1993)	Carnation (*Dianthus caryophyllus* cv. White Sim)	173	24 hours - Dark fumigation of cut flowers	Vase life (petal senescence) significantly decreased
	Carnation (*Dianthus caryophyllus* cv. Chinera)	265	24 hours - Dark fumigation of cut flowers	Vase life (petal senescence) significantly decreased
	Carnation (*Dianthus caryophyllus* cv. Epomeo)	460	24 hours -Dark fumigation of cut flowers	Vase life (petal senescence) significantly decreased
Squier *et al.* (1985)	Green ash (*Fraxinus pensylvanica* L.). Seedlings.	281	28 hours - Fumigation	15% reduction of photosynthesis
	Corn (*Zea mays* L. cv. F_1 hybrid Early Golden Giant). Seedlings	112 to 4,600	28 hours -Fumigation	No effect on photosynthesis
Ageev *et al.* (1996)	Pea (*Pisum sativum* L.). Seedlings	113.9	48 hours - Fumigation in sealed chamber	Significantly increased CO_2 evolution and alcohol dehydrogen activity relative to control
Reid *et al.* (1989)	Rose cv. "Lovely Girl"	23	2 days - Fumigation of cut flowers	Rate of flower opening inhibited b 75%

Table 9.4 Summary of effects on vegetation for ethylene exposures over 48 hours

Reference	Species Description	Ethylene ($\mu g\ m^{-3}$)	Duration and Method of Exposure	Effect
Archambault and Li (2001)	Barley (*Hordeum vulgare* cv. Harrington)	57	3 days - Fumigation	41% reduction in seed yield
	Barley (*Hordeum vulgare* cv. Harrington)	34.4	14 days - Fumigation	63% reduction in seed yield
	Canola (*Brassica napus* cv. Quantum)	57	31 days - Fumigation	20% reduction in seed yield
	Field pea (*Pisum sativum* cv. Carrera)	288	16 days - Fumigation	50% reduction in seed yield
Goeschl and Kays (1975)	Pea (*Pisum sativum* L. cv. Alaska). Etiolated seedlings	12	60 hours - Fumigation of seedlings in the dark	Inhibition of epicotyl elongation
	Bean (*Phaseolus vulgaris* L., cv. Burpee's Stringless Green Pod). Etiolated seedlings	92	60 hours - Fumigation of seedlings in the dark	Inhibition of epicotyl and root elongation, radial expansion of hypocotyl
Nowak and Fjeld (1993)	*Begonia* (2 cultivars)	173	10 days - Fumigation of mature whole plant	Flower quality and number significantly decreased
Blankenship *et al.* (1993)	Easter Lily (*Lilium longiflorum* Thunb. cv Nellie White).	58	77 days - Fumigation of mature whole plant	Flowering and plant quality (marketability) significantly decreased
Reid and Watson (1985)	Canola (*Brassica campestris* L. cv. Candle). Whole plant	40	87 days - Fumigation in sealed chambers	Seed yield 63% lower than in "background" treatment (12 $\mu g\ m^{-3}$)
	Oat (*Avena sativa* L. cv. Random). Whole plant	40	100 days - Fumigation in sealed chambers	Floret number 26% lower than in "background" treatment (8 $\mu g\ m^{-3}$)

10.0 CONCLUSION

This document has presented a summary of known information on ethylene. Section 3 described natural and anthropogenic sources of ethylene. A number of atmospheric reactions of ethylene were described in section 4 along with some processes of removal from the atmosphere. Section 5 covered methods of collecting samples, measuring and monitoring atmospheric ethylene. Ambient concentrations of ethylene in various environments were covered in section 6.

The majority of the information provided in this report was in section 7, on the effects of ethylene on vegetation. Vegetation is considered to be the most sensitive receptor. This section also covered the results of the Alberta Ethylene Crop Research Project, a joint project between the petrochemical industry and the provincial government. This project was designed to obtain information on the effects of ethylene on plant species relevant to Alberta.

Human health effects were addressed in section 8. Finally, section 9 summarized air quality guidelines in other jurisdictions and presented two tables that summarize the effects of ethylene on vegetation that can be grown in Alberta.

11.0 LITERATURE CITED

Abeles FB (1973) *Ethylene in Plant Biology.* Academic Press, New York, NY. 302 pp

Abeles FB (1982) Ethylene as an air pollutant. Agricul. For. Bull. 5(1):4-12

Abeles FB, Craker LE, Forrence LE, Leather GR (1971). Fate of air pollutants: removal of ethylene, sulfur dioxide, and nitrogen dioxide by soil. Science 173:914-916

Abeles FB, Heggestad HE (1973) Ethylene: an urban air pollutant. J. Air Pollut. Control Assoc. 23:517-521

Abeles FB, Morgan PW, Saltveit ME, Jr (1992) *Ethylene in Plant Biology, 2nd Edition.* Academic Press, Inc., San Diego CA. 414 pp

Ageev BG, Astafurova TP, Ponomarev YN, Sapozhnikova VA, Zaitseva TA, Zotikova AP (1996) Dark respiration under low pressure and increased ethylene. J. Plant Physiol. 148:237-242

Alberta Energy and Utilities Board (2001) Upstream Petroleum Industry Flaring report for year ending Dec 31, 2000. Statistical series 2001-60B. World-Wide-Web Site "www.eub.gov.ab.ca"

Altshuller AP, Lonneman WA, Sutterfield FD, Kopczynski SL (1971) Hydrocarbon composition of the atmosphere of the Los Angeles Basin – 1967. Environ. Sci. Technol. 5:1009-1016

Apel EC, Calvert JG, Zika R, Rodgers MO, Aneja VP, Meagher JF, Lonneman WA (1995) Hydrocarbon measurements during the 1992 Southern Oxidants Study Atlanta Intensive: protocol and quality assurance. J. Air Waste Manage. Assoc. 45:521-528

Archambault D, and Li X, (1999a) Report I. Design and Performance of ARC's ethylene exposure system. Alberta Research Council

Archambault D, and Li X, (1999b) Report II. The effects of ethephon on barley, wheat, oats, field peas and canola: *A screening test for the determination of ethylene sensitivity.* Alberta Research Council

Archambault D, and Li X, (2001) Report III. Response of barley, field pea, canola and tree seedlings to ethylene exposure. Alberta Research Council

Arnts RR, Meeks SA (1981) Biogenic hydrocarbon contribution to the ambient air of selected areas. Atmos. Environ. 15:1643-1651

Atkinson R (1994) Gas-phase tropospheric chemistry of organic compounds. *In: Journal of Physical and Chemical Reference Data Monograph No. 2.* American Institute of Physics; American Chemical Society, USA. pp 216

Atkinson R (1995) Initiation of chemical removal processes. *In:* Bandy AR (*Ed.*) *The Chemistry of the Atmosphere – Oxidants and Oxidation in the Earth's Atmosphere.* The Royal Society of Chemistry, Great Britian. pp 23-35

Atkinson R, Baulch DL, Cox RA, Hampson Jr RF, Kerr JA, Troe J (1992) Evaluated kinetic and photochemical data for atmospheric chemistry supplement IV: IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. J. Phys. Chem. Ref. Data 21:1125-1550

Barker Allen (1999) Ammonium accumulation and ethylene evolution by tomato infected with root-knot nematode and grown under different regimes of plant nutrition. Commun. Soil Sci. Plant Anal. 30 (1&2) 175-182

Beltrano J, Ronco MG, Montaldi ER (1999) Drought stress syndrome in wheat is provoked by ethylene evolution imbalance and reversed by rewatering, Aminoethoxyvinylglycine, or sodium benzoate. Plant Growth Regul. 18:59-64

Bausher MG (1991) Decline of *Citrus* Due to Presence of Landfill Gases in the Soil. Bull. Environ. Contam. Toxicol. 47:165-172

Baxter BJM, van Staden J, Granger JE, Brown NAC (1994) Plant-derived smoke and smoke extracts stimulate seed germination of the fire-climax grass *Themeda triandra*. Env. Exp. Bot. 34:217-223

Bernardo-Bricker A, Farmer C, Milne P, Riemer D, Zika R, Stoneking C (1995) Validation of speciated nonmethane hydrocarbon compound data collected during the 1992 Atlanta Intensive as part of the Southern Oxidants Study (SOS). J. Air Waste Manage. Assoc. 45:591-603

Beyer Jr. EM (1984) Ethylene metabolism. *In:* Roberts J, Tucker G (eds.) *Ethylene and Plant Development.* Butterworths, London. pp 125-137

Bidleman TF (1988) Atmospheric processes: wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Technol. 22:361-367

Bird CW, Lynch JM (1974) Formation of hydrocarbons by micro-organisms. Chem. Soc. Rev. 3:309-328

Blake DR, Rowland FS (1995) Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality. Science 269:953-956

Blankenship SM, Hammett LK (1987) Changes in oxygen, carbon dioxide, and ethylene mixtures stored in plastic or glass syringes. HortSci. 22:278-280

Blankenship SM, Bailey DA, Miller JE (1993) Effects of continuous, low levels of ethylene on growth and flowering of Easter lily. Sci. Hort. 53(4):311-317

Bolt HM, Filser JG (1987) Kinetics and disposition in toxicology. Example:carcinogenic risk estimate for ethylene. Arch. Toxicol. 60(1-3): 73-76

Bos R, Guicherit R, Hoogeveen A (1977) Distribution of some hydrocarbons in ambient air near Delft and the influence on the formation of secondary air pollutants. Sci. Total Environ. 7:269-281

Bottenheim JW (1984) *Plume Chemistry Studies During 1980 in the Athabasca Tar Sands Region.* Atmospheric Dispersion Division, Atmospheric Environment Service, Environment Canada, Downsview ON. Prepared for AB Environment, Project AS 3.5.6. 259 pp

Boubel RE, Darley EF, Schuck EA (1969) Emissions from burning grass stubble and straw. J. Air Pollut. Control Assoc. 19:497-500

Brymer DA, Ogle LD, Jones CH, Lewis DL (1996) Viability of using SUMMA polished canisters for the collection and storage of parts per billion by volume level volatile organics. Environ. Sci. Technol. 30:188-195

Bufalini JJ, Walker TA, Bufalini MM (1976) Ozone formation potential of organic compounds. Environ. Sci. Technol. 10:908-912

Bunce N (1994) *Environmental Chemistry (2ed)*. Wuerz Publishing, Winnipeg, Canada. 376 pp

Burford JR (1975) Ethylene in grassland soil treated with animal excreta. J. Environ. Qual. 4:55-57

Campbell RB, Moreau RA (1979) Ethylene in a compacted field soil and its effect on growth, tuber quality, and yield of potatoes. Am. Potato J. 56:199-210

Canadian Council of Ministers of the Environment (1993) Environmental Code of Practice for the Measurement and Control of Fugitive VOC Emissions from Equipment Leaks. Pub. No. CCME-EPC-73E. Canadian Council of Ministers of the Environment , Winnipeg MB. 44 pp.

Carotti AA, Kaiser ER (1972) Concentrations of twenty gaseous chemical species in the flue gas of a municipal incinerator. J. Air Pollut. Control Assoc. 22:248-253

Carter WPL (1995) Computer modelling of environmental chamber measurements of maximum incremental reactivities of volatile organic compounds. Atmos. Environ. 29:2513-2527

Carter WPL (2000) Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment. Volume 1 of 2 documentation text. California Air Resources Board

Cavanagh LA, Schadt CF, Robinson E (1969) Atmospheric hydrocarbon and carbon monoxide measurements at Point Barrow, Alaska. Environ. Sci. Technol. 3:251-257

Cheng L, Fu L, Angle RP, Sandhu HS (1997) Seasonal variations of volatile organic compounds in Edmonton, Alberta. Atmos. Environ. 31:239-246

Clean Air Strategic Alliance (1998) Alberta Ambient Air Data Management System World-Wide-Web Site "www.casadata.org/"

Colbeck I, Harrison RM (1985) The concentrations of specific $C_2 - C_6$ hydrocarbons in the air of NW England. Atmos. Environ. 19:1899-1904

Conkle JP, Camp BJ, Welch BE (1975) Trace composition of human respiratory gas. Arch. Environ. Health 30:290-295

Considine DM, Considine GD (Eds.) (1995) *Van Nostrand's Scientific Encyclopedia*, 8th Edition. Van Nostrand Reinhold, Toronto. pg. 1182.

Cook RJ, Smith AM (1977) Influence of water potential on production of ethylene in soil. Can. J. Microbiol. 23:811-817

Crossett RN, Campbell DJ (1975) The effects of ethylene in the root environment upon the development of barley. Plant Soil 42:453-464

Darley EF, Burleson FR, Mateer EH, Middleton JT, Osterli VP (1966) Contribution of burning of agricultural wastes to photochemical air pollution. J. Air Poll. Contr. Assoc. 16:685-690

Darnall KR, Lloyd AC, Winer AM, Pitts JN Jr. (1976) Reactivity scale for atmospheric hydrocarbons based on reaction with hydroxyl radicals. Environ. Sci. Technol. 10:692-696

DaSilva EJ, Henriksson E, Henriksson LE (1974) Ethylene production by fungi. Plant Sci. Lett. 2:63-66

Dean, John A. (1985) *Lange's Handbook of Chemistry, 13th Ed.* McGraw-Hill Book Co., U.S.A.

De Greef J, De Proft M, De Winter F (1976) Gas chromatographic determination of ethylene in large air volumes at the fractional parts-per-billion level. Anal. Chem. 48:38-41

Derwent RG, Jenkin ME, Saunders SM (1996) Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions. Atmos. Environ. 30:181-199

Diesburg KL, Christians NE, Gladon RJ (1989) A continuous air-exchange roomette and gas-meting system. Crop Sci. 29:344-348

Dodds JH, Musa LK, Jerie PH, Hall MA (1979) Metabolism of ethylene to ethylene oxide by cell-free preparations from *Vicia faba* L. Plant Sci. Lett. 17:109-114

Doskey PV, Porter JA, Scheff PA (1992) Source fingerprints for volatile non-methane hydrocarbons. J. Air Waste Manage. Assoc. 42:1437-1445

Egley GH (1980) Stimulation of common cocklebur (*Xanthium pensylvanicum*) and redroot pigweed (*Amaranthus retroflexus*) seed germination by injections of ethylene into soil. Weed Sci. 28:510-514

Eisele FL, Tanner DJ (1991) Ion-assisted tropospheric OH measurements. J. Geophys. Res. 96:9295-9308

El-Beltagy AS, Hall MA (1974) Effect of water stress upon endogenous ethylene levels in *Vicia faba*. New Phytol. 73:47-60

Environment Canada (1993) *National Pollution Release Inventory.* Pollution Data Branch, Environment Canada. World-Wide-Web Site "http://www.doe.ca/pdb/npri.html"

Environment Canada (1994) *National Pollution Release Inventory.* Pollution Data Branch, Environment Canada. World-Wide-Web Site "http://www.doe.ca/pdb/npri.html"

Environment Canada (1995) *National Pollution Release Inventory.* Pollution Data Branch, Environment Canada. World-Wide-Web Site "http://www.doe.ca/pdb/npri.html"

Environment Canada (2000) *National Pollution Release Inventory.* Pollution Data Branch, Environment Canada. World-Wide-Web Site "http://www.doe.ca/pdb/npri.html"

Fearn JC, LaRue TA (1991) Ethylene inhibitors restore nodulation of *sym*5 mutants of *Pisum sativum* L. cv. "Sparkle." Plant Physiol. 95:239-244

Finlayson SA, Reid DM (1994) Influence of CO_2 on ACC oxidase activity from roots of sunflower (*Helianthus annuus*) seedlings. Phytochem. 35:847-851

Finlayson-Pitts BJ, Pitts Jr JN (1986) *Atmospheric Chemistry: Fundamentals and Experimental Techniques*. John Wiley & Sons, New York, USA. 1098 pp

Flores F, Ben Amor M, Jones B, Pech JC, Bouzayen M, Latche A, Romojaro F (2001) The use of ethylene-suppressed lines to assess differential sensitivity to ethylene of the various ripening pathways in Cantaloupe melons. Phys. Plant. 113:128-133

Foster KR, Reid DM, Pharis RP (1992) Ethylene biosynthesis and ethephon metabolism and transport in barley (*Hordeum vulgare* L.). Crop Sci. 32:1345-1352

Foster, KR, Taylor, JS (1993) Response of barley to ethephon: effects of rate, nitrogen and irrigation. Crop Sci. 33:123-131

Galliard T, Grey TC (1969) A rapid method for the determination of ethylene in the presence of other volatile natural products. J. Chromatogr. 41:442-445

Gerakis PA, Veresoglou DS, Sfakiotakis E (1978) Ethylene pollution from wheat stubble burning. Bull. Environ. Contam. Toxicol. 20:657-661

Gertler AW, Fujita EM, Pierson WR, Wittorff DN (1996) Apportionment of NMHC tailpipe vs non-tailpipe emissions in the Fort McHenry and Tuscarora Mountain tunnels. Atmos. Environ. 30:2297-2305

Giannovario JA, Grob RL, Rulon PW (1976) Analysis of trace pollutants in the air by means of cryogenic gas chromatography. J. Chromatogr. 121:285-294

Goeschl JD, Kays SJ (1975) Concentration dependencies of some effects of ethylene on etiolated pea, peanut, bean, and cotton seedlings. Plant Physiol. 55:670-677

Goldstein AH, Daube BC, Munger JW, Wofsy SC (1995) Automated in-situ monitoring of atmospheric non-methane hydrocarbon concentrations and gradients. J. Atmos. Chem. 21:43-59

Goodlass G, Smith KA (1979) Effects of ethylene on root extension and nodulation of pea (*Pisum sativum* L.) and white clover (*Trifolium repens* L.) Plant Soil 51:387-395

Gordon RJ, Mayrsohn H, Ingels RM (1968) $C_2 - C_5$ hydrocarbons in the Los Angeles atmosphere. Environ. Sci. Technol. 2:1117-1120

Govindarajan AG, Poovaiah BW (1982) Effect of root zone carbon dioxide enrichment on ethylene inhibition of carbon assimilation in potato plants. Physiol. Plant. 55:465-469

Graham JH, Linderman RG (1981) Effect of ethylene on root growth, ectomycorrhiza formation, and *Fusarium* infection of Douglas-fir. Can. J. Bot. 59:149-155

Greenwood P, Greenhalgh A, Baker C, Unsworth M (1982). A computer-controlled system for exposing field crops to gaseous air pollutants. Atmos. Environ. 16:2261-2266

Grosjean E, Grosjean D, Rasmussen RA (1998) Ambient concentrations, sources, emission rates, and photochemical reactivity of C2-C10 hydrocarbons in Porto Alegre, Brazil. Environ. Sci. Technol. 32:2061-2069

Grossmann K, and Hansen H (2001) Ethylene-triggered abscisic acid: A principle in plant growth regulation? Physiol. Plant. 113: 9-14

Hanan JJ (1973) Ethylene dosages in Denver and marketability of cut-flower carnations. J. Air Pollut. Control Assoc. 23:522-524

Hanson AD, Kende H (1975) Ethylene-enhanced ion and sucrose efflux in morning glory flower tissue. Plant Physiol. 55:663-669

Harbourne CLA, McCambley WH, Trollope TJ (1973) The measurement of traces of ethylene in the atmosphere. Proc. 3rd Int. Clean Air Congr. C38-C41

Harren FJM, Reuss J, Woltering EJ, Bicanic DD (1990) Photoacoustic measurements of agriculturally interesting gases and detection of C_2H_4 below the ppb level. Appl. Spectroscopy 44:1360-1368

Harrison RM, Holman CD (1980) Some measurements of low molecular weight hydrocarbons in an area with petrochemical industrialisation. Environ. Technol. Lett. 1:345-354

Hatakeyama S, Lai H, Murano K (1995) Formation of 2-hydroxyethyl hydroperoxide in an OH-initiated reaction of ethylene in air in the absence of NO. Environ. Sci. Technol. 29:833-835

Health Canada (2001) Proposed Regulatory Decision Document PRDD2001-04 Ethylene, Eco Sprout Guard. Pest Management Regulatory Agency, 23 pp.

Heck WW, Tingey DT, Taylor OC (*Eds.*) (1988) *Assessment of Crop Loss From Air Pollutants.* Elsevier Applied Science, London. 552 pp

Hendrey GR (*Ed.*) (1993) *FACE: Free-Air CO_2 Enrichment for Plant Research in the Field.* C.K. Smoley, Boca Raton, FL. 308 pp

Hendrey GR, Lewin KF, Kolber Z, Evans LS (1992) Controlled enrichment system for experimental fumigation of plants in the field with sulfur dioxide. J. Air Waste Manage. Assoc. 42:1324-1327

Hewitt CN, Kok GL (1991) Formation and occurrence of organic hydroperoxides in the troposphere: laboratory and field observations. J. Atmos. Chem. 12:181-194

Horton RF, Bourguoin N (1992) Leaf senescence in juvenile ivy. Plant Physiol. Biochem. 30:119-122

Howard CJ (1976) Rate constants for the gas-phase reactions of OH radicals with ethylene and halogenated ethylene compounds. J. Chem. Phys. 65:4771-4777

Hunter WJ (1993) Ethylene production by root nodules and effect of ethylene on nodulation in *Glycine max*. Appl. Env. Microbiol. 59:1947-1950

Hyodo H (1991) Stress/wound ethylene. *In:* Mattoo AK, Suttle JC (eds.) *The Plant Hormone Ethylene.* CRC Press, Boca Raton FL. pp 43-64

Imaseki H (1991) The biochemistry of ethylene biosynthesis. *In:* Mattoo AK, Suttle JC (eds.) *The Plant Hormone Ethylene.* CRC Press, Boca Raton FL. pp 1-20

Institute for Research in Construction (2000) Construction Inovation Vol. 5, No. 4 Fall issue

Jackson MB, Drew MC, Giffard S (1981) Effects of applying ethylene to the root system of *Zea mays* on growth and nutrient concentration in relation to flooding tolerance. Physiol. Plant. 52:23-28

Jäger AK, Strydom A, van Staden J (1996) The effect of ethylene, octanoic acid and a plant-derived smoke extract on the germination of light-sensitive lettuce seeds. Plant Growth Regul. 19:197-201

Jerman RI, Carpenter LR (1968) Gas chromatographic analysis of gaseous products from the pyrolysis of solid municipal waste. J. Gas Chromatog. 6:298-301

Kapuya JA, Hall MA (1977) Diurnal variations in endogenous ethylene levels in plants. New Phytol. 79:233-237

Kauppi M, Kauppi A, Garty J (1998) Ethylene produced by the lichen *Cladina stellaris* exposed to sulphur and heavy-metal-containing solutions under acidic conditions. New Phytol. 139:537-547

Kays SJ, Crocker TF, Worley RE (1975) Concentration dependencies of ethylene on shuck dehiscence and fruit and leaf abscission of *Carya illinoensis* [Wang.] K. Koch. J. Agric. Food Chem. 23:1116-1118

Kays SJ, Pallas JE Jr (1980) Inhibition of photosynthesis by ethylene. Nature 285:51-52

Kende H, Baumgartner B (1974) Regulation of aging in flowers of *Ipomoea tricolor* by ethylene. Planta 116:279-289

Kevers C, Vanden Driessche T, Gaspar T (1986) An ethylene-forming system in *Acetabularia mediterranea*. Relationship with development. Arch. Int. Physiol. Biochim. 94:51

Khalil MAK, Rasmussen RA (1992) Forest hydrocarbon emissions: relationships between fluxes and ambient concentrations. J. Air Waste Manage. Assoc. 42:810-813

Kirchstetter TW, Singer BC, Harley RA, Kendall GR, Chan W(1996) Impact of oxygenated gasoline use on California light-duty vehicle emissions. Environ. Sci. Technol. 30:661-670

Kniel L, Winter O, Stork K (1980) *Ethylene. Keystone to the Petrochemical Industry*. Marcel Dekker, Inc., New York. 173 pp.

Konings H, Jackson MB (1979) A relationship between rates of ethylene production by roots and the promoting or inhibiting effects of exogenous ethylene and water on root elongation. Z. Pflanzenphysiol. Bd. 92:385-397

Kopzynski SL, Lonneman WA, Winfield T, Seila R (1975) Gaseous pollutants in St. Louis and other cities. J. Air Pollut. Control Assoc. 25:251-255

Kume A, Tsuboi N, Nakatani N, Nakane K, Sakurai N, Nakagawa N, Sakugawa H (2000) Measurement of ethylene emission from Japanese red pine (*Pinus densiflora*) under field conditions in NO_x-polluted areas. Environ. Poll. 111: 389-394

Lamb A, Larson KA, Tollefson EL (1973) A gas chromatographic method for exhaust gas analysis. J. Air Pollut. Control Assoc. 23:200-202

Lambton Industrial Society (1983) *1983 Annual Report*. Suite 2125, 242A Indian Road South, Sarnia ON N7T 3W4. 20 pp

Laurila T, Hakola H (1996) Seasonal cycle of C_2-C_5 hydrocarbons over the Baltic Sea and northern Finland. Atmos. Environ. 30:1597-1607

Lee RF, Baker J (1992) Ethylene and ethane production in an estuarine river: formation from the decomposition of polyunsaturated fatty acids. Marine Chem. 38:25-36.

Lee T-M, Chu C (1992) Ethylene-induced polyamine accumulation in rice (*Oryza sativa* L.) coleoptiles. Plant Physiol. 100:238-245

Lee K, LaRue TA (1992a) Pleiotropic effects of *sym*17. A mutation in *Pisum sativum* L. cv Sparkle causes decreased nodulation, altered root and shoot growth and increased ethylene production. Plant Physiol. 100:1326-1333

Lee KH, LaRue TA (1992b) Exogenous ethylene inhibits nodulation of *Pisum sativum* L. cv Sparkle. Plant Physiol. 100:1759-1763

Lindberg T, Granhall U, Berg B (1979) Ethylene formation in some coniferous forest soils. Soil Biol. Biochem. 11:637-643

Lonneman WA, Kopczynski SL, Darley PE, Sutterfield FD (1974) Hydrocarbon composition of urban pollution. Environ. Sci. Technol. 8:229-236

Lonneman WA, Seila RL, Bufalini JJ (1978) Ambient air hydrocarbon concentrations in Florida. Environ. Sci. Technol. 12:459-463

Lurie S, Garty J (1991) Ethylene production by the lichen *Ramalina duriaei*. Ann. Bot. 68:317-320

Lynch JM, Harper SHT (1980) Role of substrates and anoxia in the accumulation of soil ethylene. Soil Biol. Biochem. 12:363-367

Maillard P, Thepenier C, Gudin C (1993) Determining an ethylene biosynthesis pathway in the unicellular green alga, *Haematococcus pluvialis*: Relationship between growth and ethylene production. J. Appl. Phycol. 5:93-98

Martin JK, Sinnaeve J (1987) Removal of ethylene from the atmosphere of controlled environment chambers operated with full air recirculation. Soil Biol. Biochem. 19:651

Mattoo AK, White WB (1991) Regulation of ethylene biosynthesis. *In:* Mattoo AK, Suttle JC (eds.) *The Plant Hormone Ethylene.* CRC Press, Boca Raton FL. pp 21-42

McKenzie LM, Hao WM, Richards GN, Ward DE (1995) Measurement and modelling of air toxins from smoldering combustion of biomass. Environ. Sci. Technol. 29:2047-2054

Menzies RT, Shumate MS (1976) Remote measurements of ambient air pollutants with a bistatic laser system. Appl. Optics 15:2080-2084

Mohan Rao AM, Netravalkar AJ, Arora PK, Vohra KG (1983) Determination of ethylene and other reactive hydrocarbons in the atmospheric air at Trombay, Bombay by gas chromatography using a chemiluminescent detector. Atmos. Environ. 17:1093-1097

Nassar J, Goldbach J (1979) Sources and time-variations of reactive hydrocarbon emissions in the atmosphere of different industrial and rural areas. Intern. J. Environ. Anal. Chem. 6:145-169

National Research Council of Canada (1985) *Ethylene in the Environment: Scientific Criteria for Assessing its Effects on Environmental Quality.* Associate Committee on Scientific Criteria for Environmental Quality, Subcommittee on Air. NRCC Publication No. 22496. 183 pp

Neligan RE, Mader PP, Chambers LA (1961) Exhaust composition in relation to fuel composition. J. Air Pollut. Control Assoc. 11:178

Nelson PF, Quigley SM (1982) Non-methane hydrocarbons in the atmosphere of Sydney, Australia. Environ. Sci. Technol. 16:650-655

Netravalkar AJ, Mohan Rao AM (1984) Seasonal variations in the concentrations of ethylene, acetylene and propylene at Trombay, Bombay. Sci. Total Environ. 35:33-40

Niki H, Maker PD, Savage CM, Breitenbach LP (1983) Atmospheric ozone-olefin reactions. Environ. Sci. Technol. 17:312A-322A

Nowak J, Fjeld T (1993) Light and ethylene effects on assimilate distribution, acid invertase activity and keeping quality of begonia. Plant Growth Regul. 13:47-53

O'Donnell PJ, Calvert C, Atzorn R, Wasternack C, Leyser HMO, Bowles, DJ (1996) Ethylene as a signal meditating the wound response of tomato plants. Science 274:1914-1917

Oliver KD, Adams JR, Daughtrey EH Jr, McClenny WA, Yoong MJ, Pardee MA (1996) Technique for monitoring ozone precursor hydrocarbons in air at photochemical assessment monitoring stations: sorbent preconcentration, closed-cycle cooler cryofocusing, and GC-FID analysis. Atmos. Environ. 30:2751-2757

Ott S, Zwoch I (1992) Ethylene production by lichens. Lichenologist 24:73-80

Pallaghy CK, Raschke K (1972) No stomatal response to ethylene. Plant Physiol. 49:275-276

Pallas JE Jr, Kays SJ (1982) Inhibition of photosynthesis by ethylene – a stomatal effect. Plant Physiol. 70:598-601

Pearce DME, Hall KC, Jackson MB (1992) The effects of oxygen, carbon dioxide and ethylene on ethylene biosynthesis in relation to shoot extension in seedlings of rice (*Oryza sativa*) and barnyard grass (*Echinochloa oryzoides*). Ann. Bot. 69:441-447

Perkins TD Hemmerlein MT, Vogelmann HW (1993) Techniques for pollution monitoring in remote sites: II. Ozone. Water Air Soil Pollut. 68:391-397

Posthumus AC (1980) Elaboration of a communitive methodology for the biological surveillance of the air quality by the evaluation of the effects on plants. Commission of the European Communities, Belgium. CEC Report Eur 6642 EN. 40 pp

Primrose SB (1979) A review. Ethylene and agriculture: the role of the microbe. J. Appl. Bacteriol. 46:1-25

Prinn R, Cunnold D, Simmonds P, Alyea F, Boldi R, Crawford A, Fraser P, Gutzler D, Hartley R, Rosen R, Rasmussen R (1992) Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chlorofrom) data for 1978-1990. Sci. J. 97:2445-2461

Ram Chandra G, Spencer M (1963) A micro apparatus for absorption of ethylene and its use in determination of ethylene in exhaled gases from human subjects. Biochim. Biophys. Acta 69:423-425

Rasmussen RA, Khalil MAK (1982) Latitudinal distributions of trace gases in and above the boundary layer. Chemosphere 11:227-235

Reid DM, Watson K (1981) *Low Levels of Ethylene as a Phytotoxicant.* Alberta Environmental Research Trust, Alberta Environmental Protection, Alberta Canada. 49 pp

Reid DM, Watson K (1985) Ethylene as an air pollutant. *In*: Roberts JA, Tucker GA (eds.) *Ethylene and Plant Development.* Butterworths, London. pp 277-286

Reid MS, Dodge LL, Mor Y, Evans RY (1989) Effects of ethylene on rose opening. Acta Hortic. 261:215-220

Rijinders JGHM, Yang Y, Kamiya Y, Takahashi N, Barendse GWM, Blom CWPM, Voesenek LACJ (1997) Ethylene enhances gibberellin levels and petiole sensitivity in flooding-tolerant *Rumex palustris* but not in flooding-intolerant *R. acetosa* Planta 203:20-25

Robinson E (1978) Hydrocarbons in the atmosphere Pure Appl. Geophys. 116:372-384

Rogiers SY, Kumar, GN Knowles, NR (1998) Regulation of ethylene production and ripening by saskatoon (Amelanchier alnifolia Nutt.) fruit Can. J. Bot. 76:1743-1754

Rogiers SY, Knowles NR (1999) A comparison of preharvest and postharvest ethylene production and respiration rates of saskatoon (Amelanchier alnifolia Nurr.) fruit during development Can. J. Bot. 77:323-332

Rudolph J, Ehhalt DH (1981) Measurements of C_2-C_5 hydrocarbons over the north Atlantic. J. Geophys. Res. 86:11959-11964

Rudolph J, Ehhalt DH, Khedim A, Jebsen C (1981) Determination of $C_2 - C_5$ hydrocarbons in the atmosphere at low parts per 10^9 to high parts per 10^{12} levels. J. Chromatog. 217:301-310

Runeckles VC, Wright EF, White D (1990) A chamberless field exposure system for determining the effects of gaseous air pollutants on crop growth and yield. Environ. Pollut. 63:61-77

Rymen TAA (1979) Tracing organic gaseous pollutants in the atmosphere. The gas chromatographic survey of vinyl chloride- and paint industry. Intern. J. Environ. Anal. Chem. 6:1-23

Sagebiel JC, Zielinska B, Pierson WR, Gertler AW (1996) Real-world emissions and calculated reactivities of organic species from motor vehicles. Atmos. Environ. 30:2287-2296

Saito T, Yokouchi Y, Kawamura K, (2000) Distributions of C_2-C_6 hydrocarbons over the western North Pacific and eastern Indian Ocean. Atmos. Environ. 34:4373-4381

Sandberg DV, Pickford SG, Darley EF (1975) Emissions from slash burning and the influence of flame retardant chemicals. J. Air Pollut. Control Assoc. 25:278-281

Sawada S (1982) Direct application of a high sensitive gas chromatograph system to analysis of ethylene in natural atmosphere. Jap. J. Ecol. 32:441-444

Sawada S (1985) Fundamental studies on dynamics of ethylene in ecosystem. I. Atmospheric ethylene concentrations in a *Fagus crenata* forest and above paddy fields during burning of agricultural wastes. Jap. J. Ecol. 35:215-223

Sawada S, Hayakawa T, Nakahata K, Totsuka T (1986) A model calculation of ethylene removal capacity by soil acting as a natural sink in polluted atmospheres. Atmos. Environ. 20:513-516

Sawada S, Totsuka T (1986) Natural and anthropogenic sources and fate of atmospheric ethylene. Atmos. Environ. 20:821-832

Seila RL, Lonneman WA, Meeks SA (1976) Evaluation of polyvinyl fluoride as a container material for air pollution samples. J. Environ. Sci. Health, Part A 11:121-130

Seila RL, Lonneman W, Meeks S (1989) Determination of C_2 to C_{12} ambient air hydrocarbons in 39 U.S. cities, from 1984 through 1986. U.S. Environ. Prot. Agency, Off. Res. Dev. [Rep.] US EPA/600/S3-89/058.

Sexstone AJ, Mains CN (1990) Production of methane and ethylene in organic horizons of spruce forest soils. Soil Biol. Biochem. 22:135-139

Sexton K, Westberg H (1979) Ambient air measurements of petroleum refinery emissions. J. Air Pollut. Control Assoc. 29:1149-1152

Sexton K, Westberg H (1984) Nonmethane hydrocarbon composition of urban and rural atmospheres. Atmos. Environ. 18:1125-1132

Simonaitis R, Meagher JF, Bailey EM (1997) Evaluation of the condensed carbon bond (CB-IV) mechanism against smog chamber data at low VOC and NO_x concentrations. Atmos. Environ. 31:27-43

Simpson D (1995) Hydrocarbon reactivity and ozone formation in Europe. J. Atmos. Chem. 20:163-177

Singh HB, Zimmerman PB (1992) Atmospheric Distribution and Sources of Nonmethane Hydrocarbons. *In:* Nriagu, JO (ed.) *Gaseous Pollutants: Characterization and Cycling*. John Wiley & Sons, Inc., New York. pp. 182-187

Siversten B (1983) Estimation of diffuse hydrocarbon leakages from petrochemical factories. J. Air Pollut. Control Assoc. 33:323-327

Sjögren M, Li H, Rannug U, Westerholm R (1996) Multivariate analysis of exhaust emissions from heavy-duty diesel fuels. Environ. Sci. Technol. 30:38-49

Smith KA, Bremner JM, Tabatabai MA (1973) Sorption of gaseous atmospheric pollutants by soils. Soil Sci. 116:313-319

Smith KA, Restall SWF (1971) The occurrence of ethylene in anaerobic soil. J. Soil Sci. 22:430-443

Squier SA, Taylor GE Jr, Selvidge WJ, Gunderson CA (1985) Effect of ethylene and related hydrocarbons on carbon assimilation and transpiration in herbaceous and woody species. Environ. Sci. Technol. 19:432-437

Stephens ER, Burleson FR (1967) Analysis of the atmosphere for light hydrocarbons. J. Air Pollut. Control Assoc. 17:147-153

Stephens ER, Burleson FR (1969) Distribution of light hydrocarbons in ambient air. J. Air Pollut. Control Assoc. 19:929-936

Stoiber RE, Leggett DC, Jenkins TF, Murrmann RP, Rose WI Jr (1971) Organic compounds in volcanic gas from Santiaguito volcano, Guatemala. Bull. Geol. Soc. Amer. 82:2299-2302

Strosher (1996) *Investigations of Flare Gas Emissions in Alberta.* Environmental Technologies, Alberta Research Council. Calgary, AB. 145 pp

Suganuma N, Yamauchi H, Yamamoto K (1995) Enhanced production of ethylene by soybean roots after inoculation with *Bradyrhizobium japonicum.* Plant Sci. 111:163-168

Sutherland JB, Cook RJ (1980) Effects of chemical and heat treatments on ethylene production in the soil. Soil Biol. Biochem. 12:357-362

Swinnerton JW, Lamontagne RE (1974) Oceanic distribution of low-molecular-weight hydrocarbons. Environ. Sci. Technol. 8:657-663

Taylor JS, Foster KR, Caldwell CD (1991) Ethephon effects on barley in central Alberta. Can. J. Plant Sci. 71:983-995

Taylorson RB (1979) Responses of weed seeds to ethylene and related hydrocarbons. Weed Sci. 27:7-10

Tonneijck AEG, ten Berge WF, Jansen BP, Bakker C (1998) Epinastic response of potato to atmospheric ethylene near polyethylene manufacturing plants. Chemosphere 39:1617-1628

Tonneijck AEG, Jansen BP, Bakker C (2000) Assessing the effects of atmospheric ethylene on epinasty and tuber yield of potato (*Solanum tuberosum* L.) near polyethylene manufacturing plants. Environ. Mon. and Assess 60:57-69

Tosh JE, Senior E, Smith JE, Watson-Craik IA (1994) Landfill site restoration: The inimical challenges of ethylene and methane. Environ. Pollut. 83:335-340

Turner MA, Reed DW, Morgan DL (1988) Ethylene-induced defoliation in *Ficus* species and ethylene depletion by soil bacteria in peat-amended media and in vitro. J. Am. Soc. Hortic. Sci. 113:794-796

US Environmental Protection Agency (1978) *Diagnosing Vegetation Injury Caused by Air Pollution.* Report prepared by Applied Science Associates, Inc., Valencia PA for the U.S. Environmental Protection Agency. Report No. US EPA-450/3-78-005

US Environmental Protection Agency (1988) Method TO14: determination of volatile organic compounds (VOCs) in ambient air using SUMMA passivated canister sampling and gas chromatographic analysis. *In:* Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. US EPA-600/7-89-017. Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

US Environmental Protection Agency (1996) *Air Quality Criteria for Ozone and Related Photochemical Oxidants*, Volume II of III

US Environmental Protection Agency (1992) Reregistration Eligibility Document – Ethylene – Case 3071. Office of Pesticide Programs, Washington, DC

van Workum WAT, vanBrussel AAN, Tak T, Wijffelman CA, Kijne JW (1995) Ethylene prevents nodulation of *Vicia sativa* spp. *nigra* by exopolysaccharide-deficient mutants of *Rhizobium leguminosarum* bv. *viciae.* Mol. Plant Microbe Interact. 8:278-285

Verschueren, K (1983) *Handbook of Environmental Data on Organic Chemicals.* 2nd Edition. Van Nostrand Reinhold Co. New York, NY. pp. 46, 632-635

Voesenek LACJ, Harren FJM, Bögemann GM, Blom CWPM, Reuss J (1990) Ethylene production and petiole growth in *Rumex* plants induced by waterlogging. The application of a continuous flow system and a laser driven intracavity photoacoustic detection system. Plant Physiol. 94:1071-1077

Voesenek LACJ, van der Putten WH, Maun MA, Blom CWPM (1998) The role of ethylene and darkness in accelerated shoot elongation of *Ammophila breviligulata* upon sand burial.. Oecologia 115:359-365

Wang Y, Raihala TS, Jacman AP, St. John R (1996) Use of Tedlar bags in VOC testing and storage: evidence of significant VOC losses. Environ. Sci. Technol. 30:3115-3117

Warneck P (1988) *Chemistry of the Natural Atmosphere.* Academic Press, Inc., Toronto. pp. 224-226

Wayne RP (1991) *Chemistry of Atmospheres.* Clarendon Press, Oxford, UK. 324 pp

Weber A, Nieme M, Sundman V, Skuji_s V (1983) Acetylene reduction (N_2 fixation) and endogenous ethylene release in sub-boreal soils and peats of Finland. Oikos 41:219-226

Westberg HH, Rasmussen RA, Holdren M (1974) Gas chromatographic analysis of ambient air for light hydrocarbons using a chemically bonded stationary phase. Anal. Chem. 46:1852-1854

Whalen MC, Feldman LJ (1988) The effect of ethylene on root growth of *Zea mays* seedlings. Can. J. Bot. 66:719-723

Wheeler RM, Peterson BV, Sager JC, Knott WM (1996) Ethylene production by plants in a closed environment. Adv. Space Res. 18: (405)193-(405(196)

Whitby RA, Altwicker ER (1978) Acetylene in the atmosphere: sources, representative ambient concentrations and ratios to other hydrocarbons. Atmos. Environ. 12:1289-1296

Woltering EJ, Harkema H (1987) Effect of exposure time and temperature on response of carnation cut flowers to ethylene. Acta Hortic. 216:255-262

Woltering EJ, Somhorst D, de Beer CA (1993) Roles of ethylene production and sensitivity in senescence of carnation flower (*Dianthus caryophyllus*) cultivars White Sim, Chinera and Epomeo. J. Plant Physiol. 141:329-335

Woltering EJ, Van Doorn WG (1988) Role of ethylene in senescence of petals – morphological and taxonomical relationships. J. Exp. Bot. 39:1605-1616

Wong MH, Yu CT (1989a) Monitoring of Gin Drinkers' Bay landfill, Hong Kong: I. Landfill gas on top of the landfill. Environ. Manage. 13:743-752

Wong MH, Yu CT (1989b) Monitoring of Gin Drinkers' Bay landfill, Hong Kong: II. Gas contents, soil properties, and vegetation performance on the side slope. Environ. Manage. 13:753-762

Woodrow L, Thompson RG, Grodzinski B (1988) Effects of ethylene on photosynthesis and partitioning in tomato, Lycopersicon esculentum Mill. J. Exp. Bot. 39:667-684

Wullschleger SD, Hanson PJ, Gunderson CA (1992) Assessing the influence of exogenous ethylene on electron transport and fluorescence quenching in leaves of *Glycine max*. Env. Exp. Bot. 32:449-455

Yokelson RJ, Goode JG, Ward DE, Susott RA, Babbitt RE, Wade DD, Bertschi I, Griffith DWT, Hao WM (1999) Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectoscopy. J. of Geophysical Res. 104:30,109-30,125.

Zielinska B, Sagebiel JC, Harshfield G, Gertler AW, Pierson WR (1996) Volatile organic compounds up to C_{20} emitted from motor vehicles; measurement methods. Atmos. Environ. 30:2269-2286